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# AGING OF POLYMERS AND COMPOSITES

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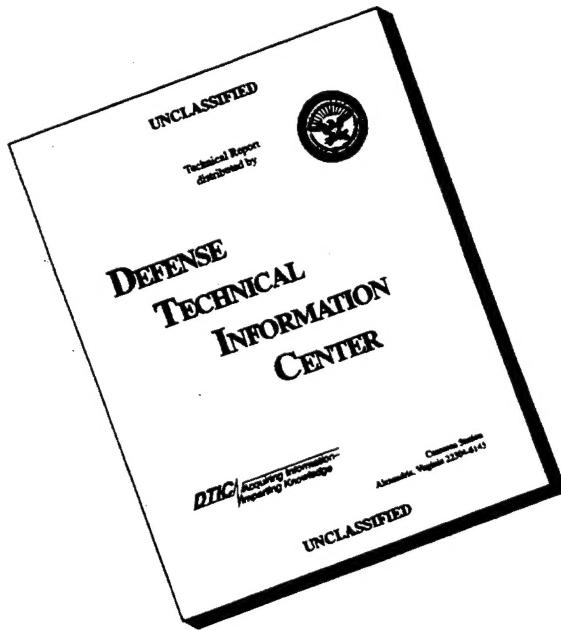
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The microchemical changes produced during the aging of the resin system, MY720 (Ciba-Geigy) cured with Eporal (Ciba-Geigy), were studied by the combined use of chemiluminescence, vaporization gas chromatography (and mass spectrometry), precision abrasion mass spectrometry, and stress mass spectrometry. Resin coupons were aged at ambient, 85°C and 150°C in dry and moist atmospheres in the presence and absence of an external tensile stress (up to 50% of the ultimate tensile stress). The chemiluminescence		

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peak intensity which occurs at a temperature change was found to be an inverse function of the aging time for a given set of environmental parameters. Propenal, a low-temperature decomposition product of the resin, may be related to the chemiluminescence and aging processes.

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## PREFACE

This report is an account of the work performed at the McDonnell Douglas Research Laboratories on Aging of Polymers and Composites for the Naval Air Systems Command, Contract No. N00019-80-C-0102, from 21 April 1980 to 21 July 1981. The work was performed in the Chemical Physics Department, managed by Dr. D. P. Ames. The principal investigator was Dr. C. J. Wolf; coinvestigators were Mr. D. L. Fanter and Mr. M. A. Grayson. The project monitor was Mr. R. L. Dempsey, Naval Air Systems Command.

This technical report has been reviewed and is approved.

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## 1. SUMMARY

High-sensitivity physical-analytical chemical techniques were used to characterize the aging processes in the epoxy resin system, MY720 (mainly tetraglycidaldiaminodiphenyl methane, Ciba-Geigy) cured with Eporal (diaminodiphenylsulfone, Ciba-Geigy). The test coupons were exposed to accelerated aging conditions in which the temperature, humidity, and external tensile stress were varied over a considerable range. The aging conditions used in this study are summarized in Table 1. Chemiluminescence (CL) intensity-temperature-time (ITt) profiles of the aged resin were measured at four temperatures. The reciprocal of the maximum CL intensity occurring at each temperature increment was a linear function of the environmental aging period ( $\tau_A$ ). Vaporization gas chromatography (Vap GC) measurements of the aged resins indicate that propenal (acrolein) is formed during the relatively low-temperature thermal aging ( $\sim 150^\circ\text{C}$ ). The activation energies for the CL process and propenal production are similar, approximately 90-105 kJ/mol, and suggest that the reaction(s) forming propenal may be involved in the production of CL. Fourier transform infrared (FTIR) spectrometry studies show the presence of a carbonyl group ( $>\text{C=O}$ ) which probably results from partial oxidation of the glycidyl moiety in the MY720. These observations are consistent with the general hypothesis that the glycidyl group is responsible for both CL and propenal production.

Stress mass spectrometry (SMS) was used to show that  $\text{SO}_2$  is released when the resin is fractured in tension. The  $\text{SO}_2$  probably is formed by decomposi-

TABLE 1. SUMMARY OF CHEMILUMINESCENCE INTENSITY-TEMPERATURE-TIME PROFILE STUDIES ON AGED EPOXY RESIN SAMPLES.

Temp ( $^\circ\text{C}$ )	Humidity		Mechanical stress		Maximum aging period
	Low*	50%	0	50% UTS	
23†	X†		X		14 months
85	X		X		29 days
85	X			X	42 days
85		X	X		196 days
85		X		X	195 days
150	X		X		34 days
150	X			X	42 days

\*Approximately 2-4%

†Ambient conditions

tion of the free radical ( $-\theta\text{SO}_2\cdot$ ) produced by main-chain bond cleavage of the resin network. The overall effect of aging on the reactions producing  $\text{SO}_2$  is not known.

The equilibrium weight of water in freshly cured resin samples was less than 0.1 wt%. However, the resin lost 2.3 to 3 wt% when aged at 150°C depending upon whether an external stress was applied. Samples exposed to a humid environment (50% RH) at 85°C in either the presence or absence of mechanical stress reached an equilibrium weight gain of 1.8 wt%.

The data indicate that the mechanism responsible for CL production in this resin system does not change appreciably within the temperature range investigated, i.e., up to 90°C. This result suggests that CL may be a good method to monitor real-time aging within the service environment.

## 2. INTRODUCTION

Polymers and composites are finding ever-increasing use as structural components in aerospace systems because of their attractive strength/weight characteristics. During the past 20 years, their use in military aircraft has increased from essentially zero in F-4 Phantom jets to over 25% in the advanced AV8-B Harrier.

Consequently, the aerospace industry has developed fabrication and testing procedures that are radically different from those traditionally used with metals. However, little is known about the long-term durability of these relatively new nonmetallic composites, and their full potential has not been realized. By most standards, these materials are considered extremely stable, and if deleterious aging reactions occur, they are slow, requiring many years to cause component failure.

Normally, accelerated aging tests are conducted by exposing the sample to a specific environment at high temperature for short periods, possibly as long as several months. The short-time, high-temperature, high-intensity data then are extrapolated to the environmental-use envelope for the corresponding long service periods. Since the aging mechanism at high temperature may not be identical to the mechanism operative at service conditions, such extrapolations are suspect; therefore the results of accelerated aging experiments are of questionable validity. Realistic test procedures and methods are required that can reliably predict the long-term properties of these materials from short-duration (weeks to months) tests.

Because of the slow reaction rates, even at accelerated conditions, sensitive procedures are required to measure these effects. Recently, new and highly sensitive physical-analytical techniques have been developed which may be useful in describing the aging processes in organic-matrix composite materials. Chemiluminescence (CL), a phenomenon in which part of the exothermicity of a chemical reaction is released as electromagnetic radiation, is an ultrasensitive technique which has great potential to measure the slow reaction rates occurring during aging.<sup>1-5</sup> In fact, it has been reported that CL is capable of measuring organic reaction rates as low as  $10^{-14}$  mol/year.<sup>1-5</sup> The potential of this method, especially when coupled with other sensitive

physical-analytical techniques, such as stress mass spectrometry,<sup>6-8</sup> vaporization gas chromatography mass spectrometry,<sup>9</sup> and precision abrasion mass spectrometry,<sup>10,11</sup> to measure and characterize the chemical aging of complex polymeric and organic resin matrix composites is promising.

During the first phase of this program, the utility of CL to monitor changes in real resin systems exposed to a controlled environment was determined. In addition, changes in the microchemical composition of these same resin systems were monitored during the aging processes.

### 3.0 EXPERIMENTAL PROCEDURE

#### 3.1 Sample Preparation

##### 3.1.1 Resin Components

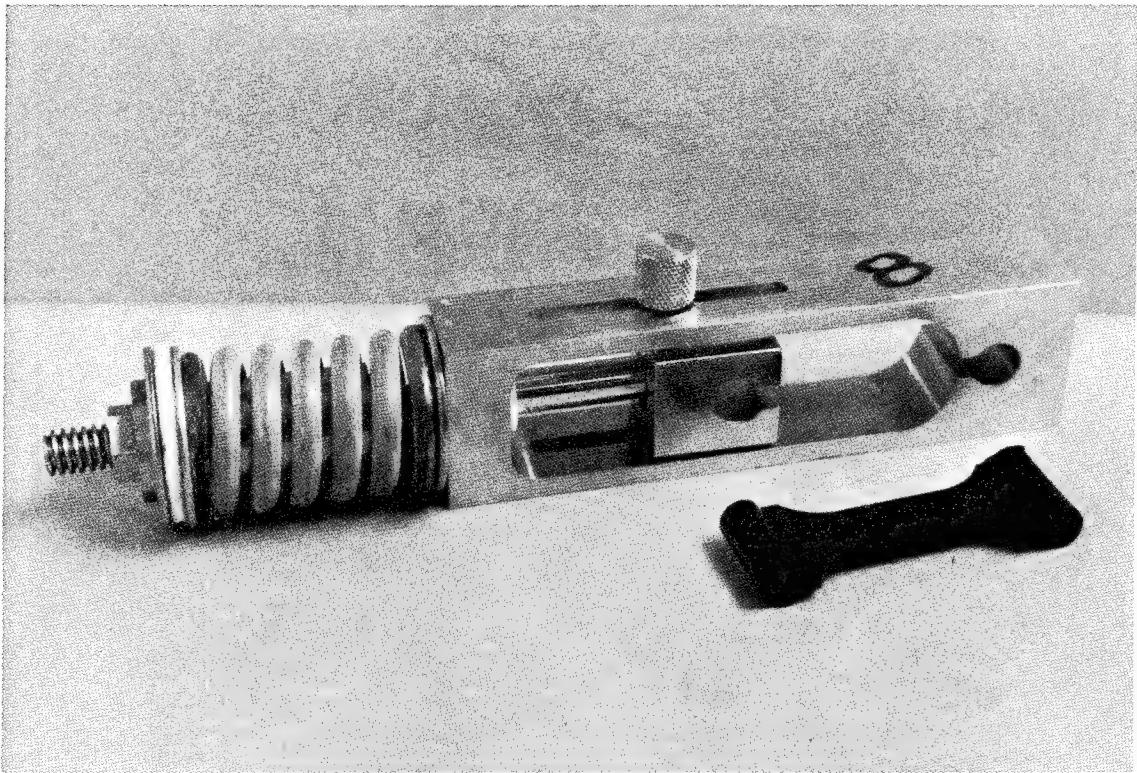
Epoxy resins used in this study were fabricated from the same components employed to prepare most of the commercially available graphite-epoxy prepreg resins used in military aircraft, namely Narmco 5208, AS 3501-6, Hercules 3501-5, and Fiberite 934. The epoxide (MY720, batch 591097, Ciba-Geigy) and amine hardener (Eporal, batch 521054, Ciba-Geigy) were obtained from the manufacturer in quantities sufficient for fabricating all samples used in the experimental program. As recommended by the manufacturer, MY720 was stored at -20°C until needed. Eporal was stored in a sealed container at room temperature until needed. For the experiments reported herein, the epoxide and hardener were used without further purification.

##### 3.1.2 Resin Preparation

Approximately 1 kg of MY720 was heated briefly to 70°C and mixed with 27 parts Eporal per hundred parts (phr) MY720. The temperature was gradually increased to 150°C while stirring to facilitate mixing. The mixture was cooled to room temperature, stored at -20°C, and used as a master batch.

##### 3.1.3 Mold Fabrication

Fifteen silicone rubber molds were cast from a master stainless steel template machined in the shape of a dogbone with gauge dimensions of 4 x 12 x 25 mm. The grip portion of the sample was terminated in a cylindrical shape. This configuration permits the use of simple, small clamps (Figure 1). The molds were cast according to the method described by Fanter.<sup>12</sup> A two-part silicone-rubber casting material (RTV-664, General Electric) was poured into a form containing the pattern and cured at room temperature for 24 h. The molds were post-cured at 177°C for 3 h.



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**Figure 1. Typical epoxy resin coupon and stress rig used to impose mechanical loads on samples during environmental exposure.**

#### **3.1.4 Casting**

The silicone-rubber molds and premixed resin were heated to 150°C prior to casting. After the Eporal was totally dissolved, the resin was deaerated in a vacuum bell jar, reheated to 150°C, and poured into the preheated molds. The samples were cured for 1 h at 150°C, followed by 5 h at 177°C; then the oven was turned off and the samples were allowed to cool slowly to room temperature.

The samples were removed from the molds, and the batch and mold numbers were inscribed on one surface. The samples were weighed and stored at room temperature in dry air until needed. A total of 120 samples were fabricated in the manner described.

#### **3.2 Environmental Aging**

The samples were aged in either an environmental exposure chamber or a constant-temperature oven. The environmental chamber (Tenney model BTRS) is

capable of operating and maintaining (up to several months) a hot, humid atmosphere which can be varied to 177°C while the relative humidity can be varied from 20 to 98% (for temperatures up to 85°C). The internal dimensions of the chamber are 0.5 x 0.5 x 0.5 m permitting the simultaneous aging of many specimens mounted in stress rigs. The temperature and humidity in the chamber were monitored by a circular chart recorder which was changed weekly.

Two constant-temperature ovens were used: 1) a Lab-Line model Imperial III which could be controlled to  $\pm 1^{\circ}\text{C}$  for temperatures up to 300°C and 2) a Varian model 1520 chromatographic oven which could be controlled to  $\pm 0.5^{\circ}\text{C}$  for temperatures up to 400°C.

### 3.3 Environmental Stress Fixtures

A mechanical load was applied to approximately half of the samples during environmental exposure using the stress rigs shown in Figure 1. A typical dogbone-shaped resin coupon is shown in the lower right of Figure 1. The shape of the molded samples matches the slots in the stress rig so that the sample can slide into the stress rig and the loading nut can be tightened to apply tension to the sample. The design of the rig and the shape of the molded samples are such that the sample is automatically aligned when it is installed in the stress rig.

The total force applied to the sample in the stress rig was determined immediately prior to loading the sample. A load transducer was installed in the stress rig, and the torque on the loading nut, which gives the desired total force on the sample, was determined. The sample was then installed in place of the load transducer, and the nut was tightened to the desired torque. The spring in the stress rig minimizes changes in tensile load during the experiment.

### 3.4 Mechanical Testing

The ultimate tensile strength (UTS) of the cured resin system was determined in a universal testing instrument (Instron model TM-SM-L). The samples were loaded in tension to failure. The UTS was  $78 \pm 6$  MPa at room temperature. To perform these measurements, the loading jaws of the instrument were replaced with the movable block portions of the stress rigs so that

the molded samples could be conveniently mounted in the universal testing instrument. The data obtained from mechanical testing were used to determine the loads applied during environmental exposure.

### 3.5 Chemical Analysis

One of the primary objectives of this program was to carefully monitor microchemical changes that occur in the resin system during the aging processes; therefore several sensitive methods were used to study the chemical composition before and after aging. A brief description of each is given. For those procedures and methods which are not relatively standard analytical methods, detailed descriptions are given in the Appendices.

#### 3.5.1 Chemiluminescence

Chemiluminescence (CL) is a relatively common phenomenon in which part of the energy of an exoergic chemical reaction is released as electromagnetic radiation, i.e., light.<sup>1,2</sup> Many reactions, such as oxidation, hydration, and acid-base, exhibit CL. In general, there are only two requirements for a reaction to be chemiluminescent: 1) the reaction must be sufficiently energetic to raise one of the reaction products to an excited state, and 2) the excited state must be sufficiently long-lived to deexcite by a radiative process.

The resin samples were analyzed immediately after removal from the environmental chamber. The coupons were inserted into the CL system at 50°C with an oxygen flow rate of 15 cm<sup>3</sup>/min. The CL intensity was measured for 1 h, and the temperature was increased to 65°C. The process was repeated at 75° and 90°C. This series of measurements constitutes an intensity-temperature-time (ITt) profile. The profiles of all aged samples were measured in the manner described above. The CL system and technique developed at MDRL are described in detail in Appendix A.

#### 3.5.2 Vaporization Gas-Chromatography/Mass-Spectrometry

Vaporization gas-chromatography/mass-spectrometry (Vap GC/MS) is a technique developed at MDRL specifically to analyze for trace compounds in an intractable matrix.<sup>9</sup> The technique has been utilized successfully to characterize the organic compounds in lunar samples<sup>13,14</sup> and meteorites.<sup>15,16</sup>

In this study, thin shavings, approximately 10-20  $\mu\text{m}$  thick, were milled from the aged resin coupons. The shavings were placed in a tared quartz tube, weighed, and connected to flowing helium in the gas chromatograph. Volatile compounds desorb from the sample shavings when they are inserted into the heated region of the Vap GC oven. The compounds are transferred by the flowing helium to an in-line low-temperature trap. The sample can be heated at any temperature from ambient to 250°C for periods as long as several hours. Chromatographic analysis is accomplished by removing the sample from the heated zone, heating the column trap, and starting the chromatographic temperature program. This technique is extremely sensitive, permitting the qualitative detection of as little as  $10^{-10}$  g of volatile compound per gram of resin. The apparatus and procedure are described in detail in Appendix B.

### 3.5.3 Stress Mass Spectrometry

Stress MS is a relatively new application of mass spectrometry to study the mechanical degradation of polymeric materials.<sup>7,8</sup> Test coupons are subjected to a stress, either mechanical or thermal, and the resultant products are analyzed mass spectrometrically.<sup>6,17</sup> The entire experiment, including application of stress, is performed directly in the ion-source housing of the mass spectrometer. A time-of-flight mass spectrometer (TOFMS) is ideally suited for these studies because it has a large, open ion source and produces 20 000 mass spectra per second. A detailed description of the system used to perform these experiments is given in Appendix C. Selected resin samples subjected to various environmental aging factors of temperature, humidity, and stress were analyzed. The 0.45 mm thick coupons were dried in a vacuum oven at 83°C for 100 h prior to analysis. All samples were strained at a rate of 0.16 mm/s prior to fracture.

### 3.5.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a relatively recent enhancement of the well-known infrared spectroscopy technique. FTIR has the advantage of utilizing higher signal-to-noise, greater light throughput to the sample, and an expanded data handling and processing capability.<sup>18</sup> However, for these solid polymeric materials, relatively thin samples are required for both conventional infrared and FTIR. The samples used in this study were from 1 to 4 mm thick; therefore the

technique of attenuated total reflection (ATR) was used in conjunction with FTIR.<sup>19</sup> In this method, the resin is placed in contact with a reflecting surface (a KRS-5 plate), and the spectrum is measured in the conventional manner. Measurements are restricted to the first 1-2  $\mu\text{m}$  of the surface layer.<sup>19</sup>

### 3.5.5 Precision Abrasion Mass Spectrometry (PAMS)

PAMS was specifically developed at MDRL to qualitatively and quantitatively characterize the distribution of indigenous volatile compounds trapped within a solid intractable polymer material.<sup>17,20,21</sup> Solid samples are abraded precisely inside the ion-source housing of a time-of-flight mass spectrometer (TOFMS). The volatile compounds released during abrasion expand into the ion source and are ionized, mass analyzed, detected, and recorded. As many as 10 ions can be monitored simultaneously. The selected ions are measured as a function of time during constant abrasion, thereby generating a spatial distribution profile. A detailed description of the system is given in Appendix D. The initial distribution of water, carbon dioxide, nitrogen and oxygen was measured in selected virgin coupons within 48 h after removal from the mold.

### 3.5.6 Liquid Chromatography

Resin coupons used throughout this program were prepared from a single batch of epoxy resin, MY720 and Eporal. These starting materials were characterized by liquid chromatography.<sup>22</sup> The analyses were conducted with a liquid chromatograph (Spectra Physics 8000) containing a 9.4 mm dia x 50 cm column (Whitman Partisil Magnum-9).

The solvent was acetonitrile/water in the gradient elution mode; the gradient ranged from 20% to 100% acetonitrile in 130 min. The MY720 was approximately 72% tetraglycidylaminodiphenyl methane and contained six other compounds, primarily higher-molecular-weight analogs and triglycidyl derivatives whose concentrations ranged from 1.5% to 14%. The Eporal was approximately 91% pure diaminodiphenyl sulfone and contained four major impurities whose concentrations ranged from less than 1% to almost 4%.

### 3.5.7 Pyrolysis Mass Spectrometry (Py-MS)

Py-MS is a recent extension of the classical pyrolysis and pyrolysis gas chromatographic methods of analysis.<sup>23</sup> In this approach, the pyrolytic fragmentation of the sample is carried out near the ion-source of a mass spectrometer, and the pyrolysis products are analyzed directly by measurement of the time-averaged mass spectrum. A double-focusing mass spectrometer (Kratos MS-30) was used for all analyses. Extensive analysis of the epoxide MY720, the amine (DDS), and various stages of cured resins showed that the Py-MS approach is not a viable method for the microchemical characterization of the epoxy resin system of interest in this program.

#### 4. RESULTS

The results of the studies on the aged epoxy resin samples are discussed below, according to the method by which the data were obtained.

##### 4.1 Chemiluminescence Studies

The CL intensity-temperature-time (ITt) profiles of resin coupons aged for various periods of time, temperature, humidity, and tensile stress were measured. A ITt profile of a resin coupon measured immediately after removal from the fabrication mold is shown in Figure 2. In this plot and all subsequent ITt profiles, the temperature (T) of the sample during CL measurement is shown by the dashed line (the temperature scale is the left ordinate), the CL intensity by the solid line (intensity flux by the right ordinate), and, on the abscissa, the time (t) after the measurement commenced.

The initial peak that occurs when the sample is inserted in the CL chamber is highly variable and depends upon many factors including the photochemical history of the sample; therefore it is not used for analysis and is disregarded. A sharp increase in CL intensity occurs each time the tempera-

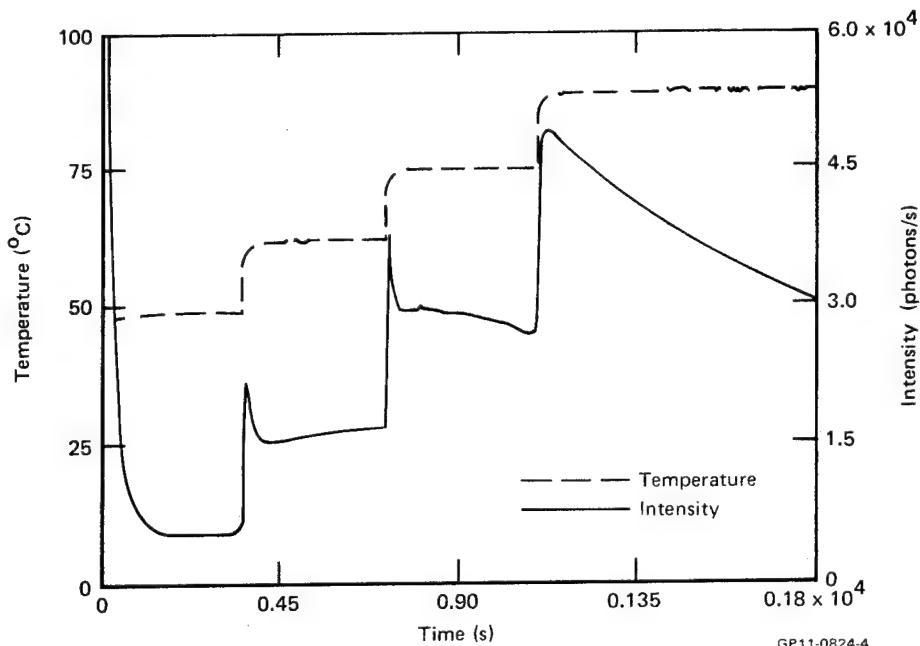


Figure 2. Chemiluminescence intensity-temperature-time profile for resin directly after removal from mold.

ture is increased; these CL peaks are specified by a subscript. For example,  $CL_{50-65}^o$  refers to the intensity of the CL peak observed when the temperature is increased from  $50^o$  to  $65^oC$ . The peaks from both the  $49^o$  to  $62^oC$  and  $62^o$  to  $74^oC$  thermal transitions are rather sharp and have half-widths of approximately 100 s. Aging, even for relatively short periods of time, broadens these peaks.

A typical ITt profile of a sample aged for 14 months at ambient conditions is shown in Figure 3; the peaks are considerably broader (half-widths approximately 600-700 s) and decay in a relatively smooth manner. For comparison, the ITt profile of the uncured resin components, MY720 and Eporal (DDS), are shown in Figures 4 and 5, respectively. The CL intensity from the unpolymerized MY720 is an order-of-magnitude greater than that observed in the cured resin. In addition, the general shape of the ITt profile is different; for example, no peak is observed when the MY720 is heated from  $90^o$  to  $120^oC$ . In fact, the intensity increases slowly after a brief initial rapid increase. The CL intensity from Eporal is small, approximately 3 orders-of-magnitude less than that observed in the MY720 and 2 orders-of-magnitude less than that found in the resin. Although the CL intensity from Eporal is low, the curve follows the same general shape noted in the resin. The differences

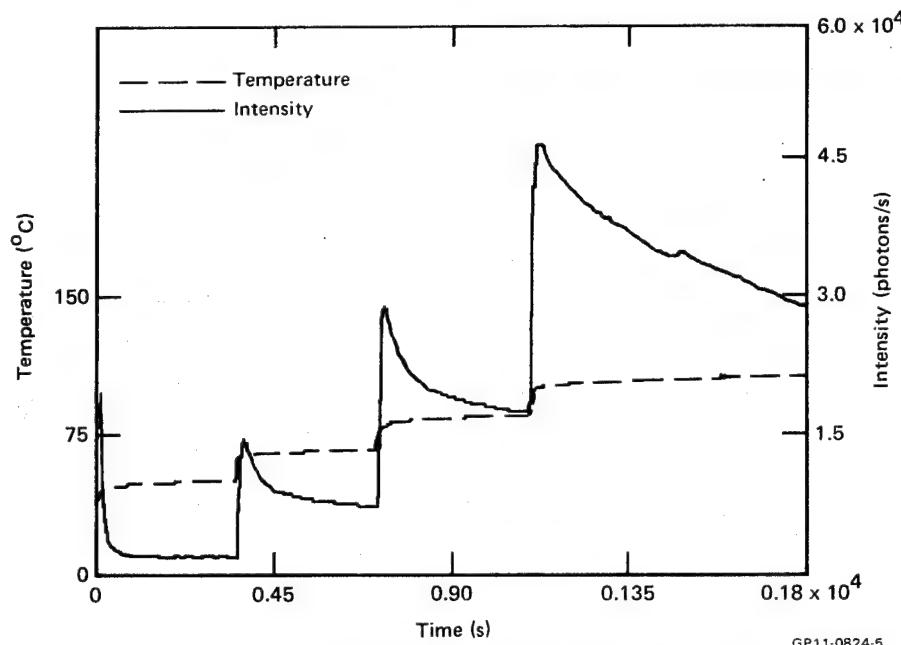
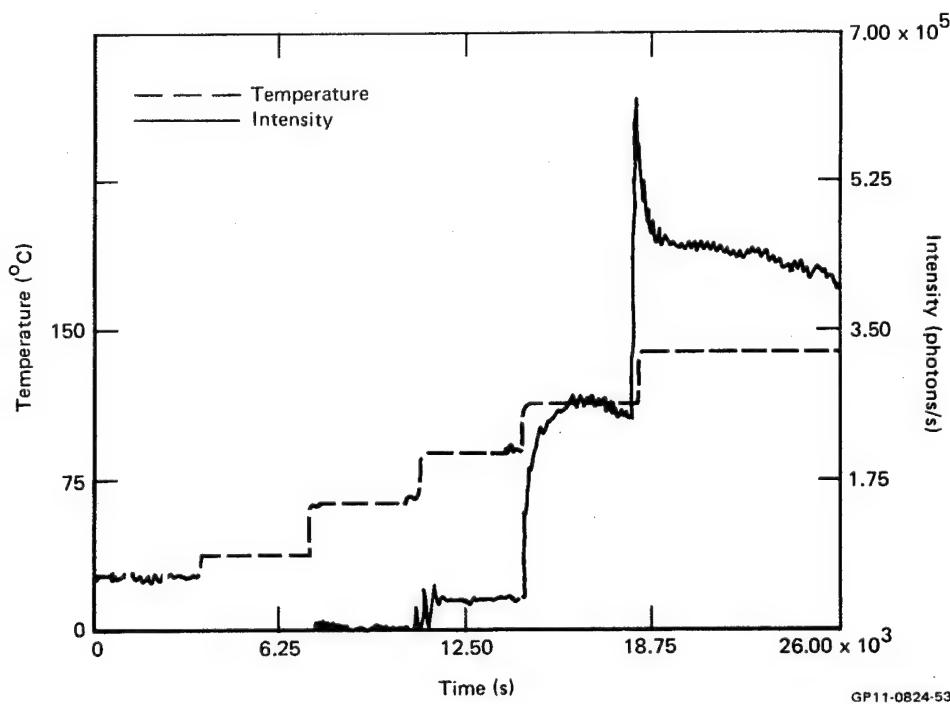
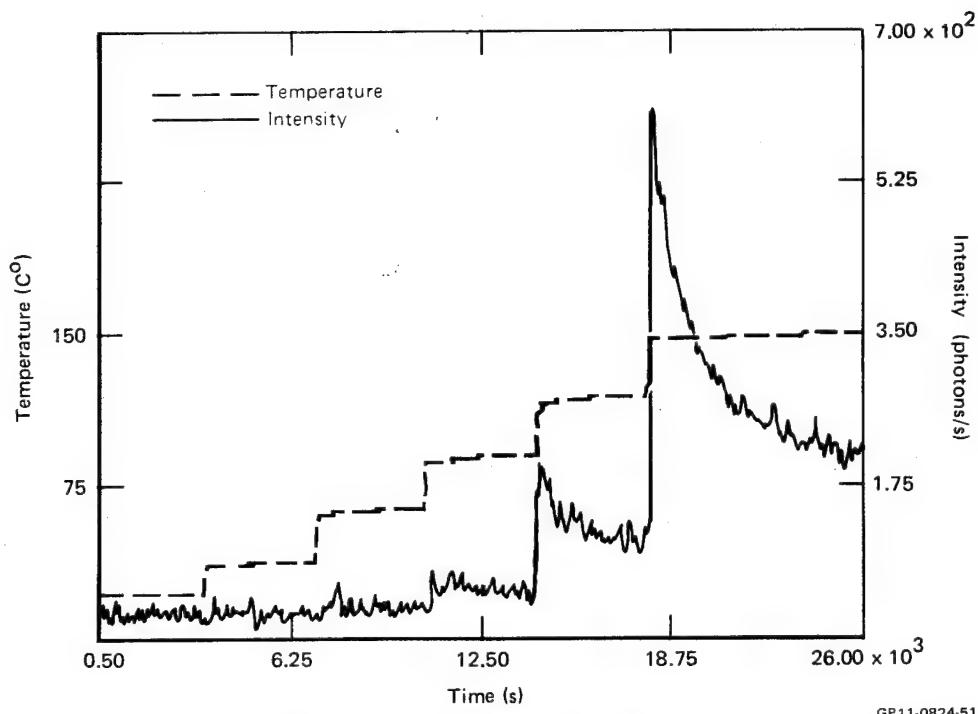


Figure 3. Chemiluminescence intensity-temperature-time profile for resin aged in the ambient environment for 14 months.

in intensity and form of the ITT profile from MY720, Eporal, and the cured resin show that the CL observed from the cured resin is a property of the resin and is not due to either unpolymerized MY720 or Eporal.



**Figure 4. Chemiluminescence intensity-temperature-time profile from as-received MY 720 epoxy.**



**Figure 5. Chemiluminescence intensity-temperature-time profile from as-received DDS.**

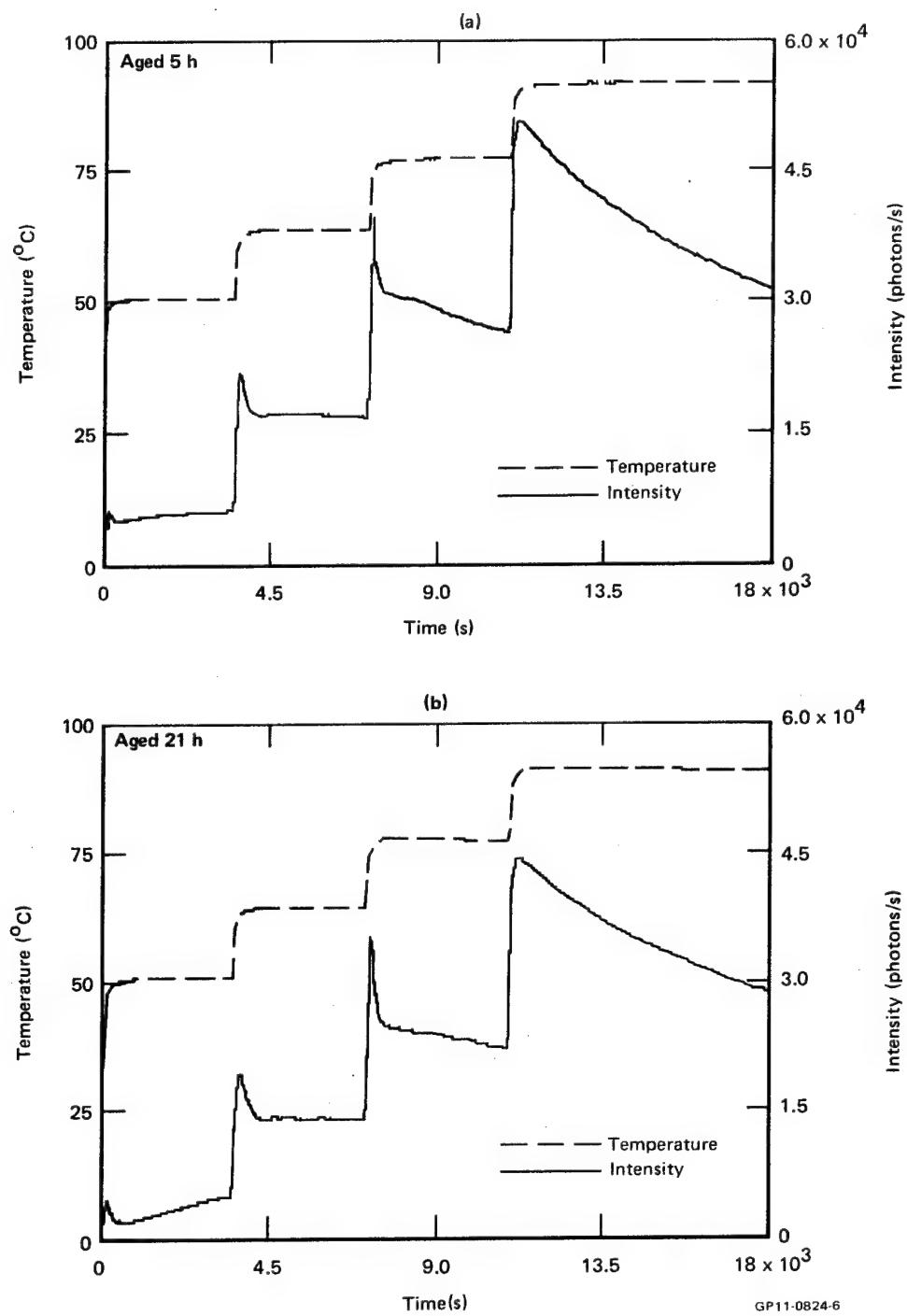
The ITt profiles for the resin aged at 85°C in an air atmosphere with 50% humidity in the absence of applied tensile stress are shown in Figure 6; samples aged for 5, 21, 50.5, 68, 168, 240, 365, 650, and 1008 h are shown in Figures 6(a-i), respectively. The CL intensity decreases as a function of aging, and the peaks change from relatively sharp spikes to much broader peaks. The CL peak intensities from the 50° to 62°C and the 62° to 76°C thermal transitions as well as the constant intensity regions, i.e., the plateau values, at 62°C and 76°C are shown in Figure 7 as a function of aging time ( $\tau_A$ ). A similar plot of the CL intensity from the 76° to 90°C peak and the intensity of the 90°C plateau as a function of aging time ( $\tau_A$ ) are shown in Figure 8. The intensity of peaks and plateaus at all temperatures is a smooth decreasing function of the aging period. The decrease suggests that CL and aging are inversely related. A plot of the reciprocal of the peak CL intensity from the 62° to 76°C thermal transition as a function of aging time ( $\tau_A$ ) is shown in Figure 9. The least-squares fit to the data is shown by the solid line, which corresponds to the equation:

$$[\text{CL} - \text{CL}_0]_{85^\circ, 50, 0}^{-1} = 2.69 \times 10^{-7} \tau_A + 2.08 \times 10^{-5}, \quad (1)$$

where CL is the intensity in photons/s,  $\text{CL}_0 = 5000$  photons/s, and time ( $\tau_A$ ) is in hours. All CL data, regardless of stress or humidity, were treated in a similar fashion.

The ITt profiles from the resin following aging at 85°C in a dry atmosphere (less than 2% RH) while subjected to a tensile stress equal to 50% UTS are shown in Figures 10(a-c) for aging periods of 167, 432, and 696 h, respectively. The CL intensity from the peak corresponding to the 62° to 75°C transition as a function of aging time is shown in Figure 10. The straight line in Figure 11 is a least-squares fit of the experimental data and is given by the equation

$$[\text{CL}]_{85, 0, 50}^{-1} = 0.99 \times 10^{-7} \tau_A + 4.35 \times 10^{-5}. \quad (2)$$



**Figure 6. Chemiluminescence intensity-temperature-time profiles for resin aged at 85°C and 50% RH in the absence of mechanical stress.**

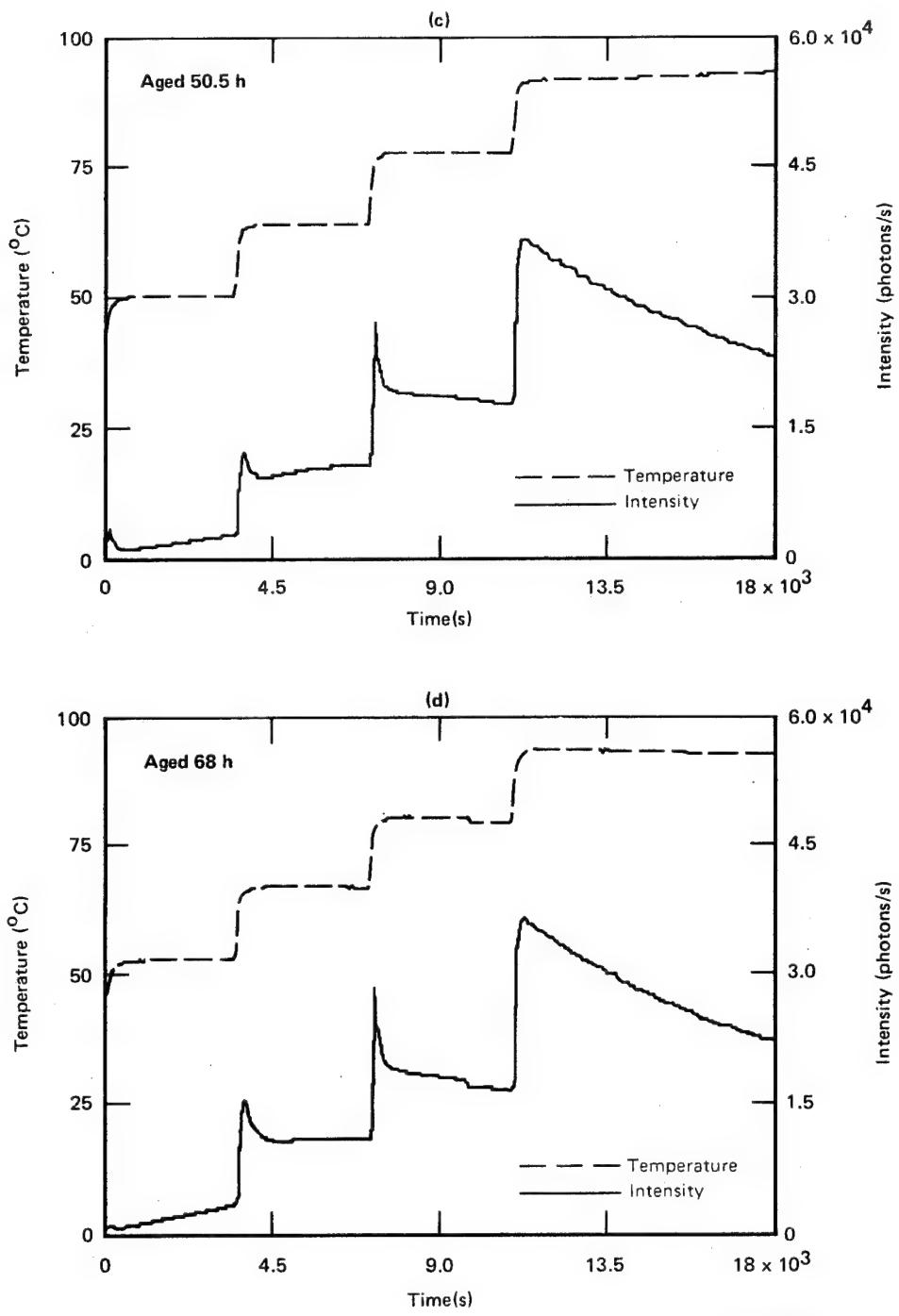


Figure 6 (cont.).

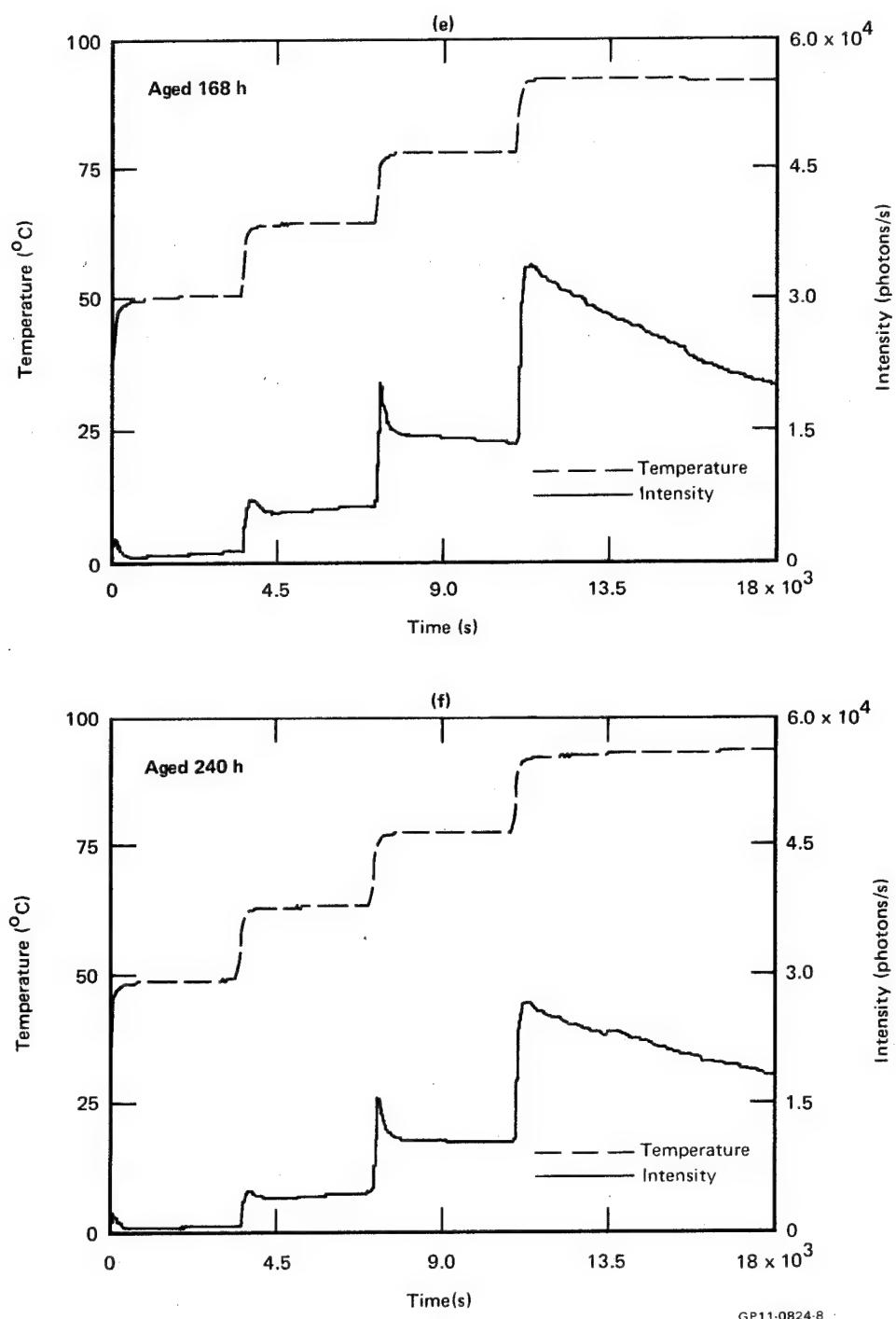


Figure 6 (cont).

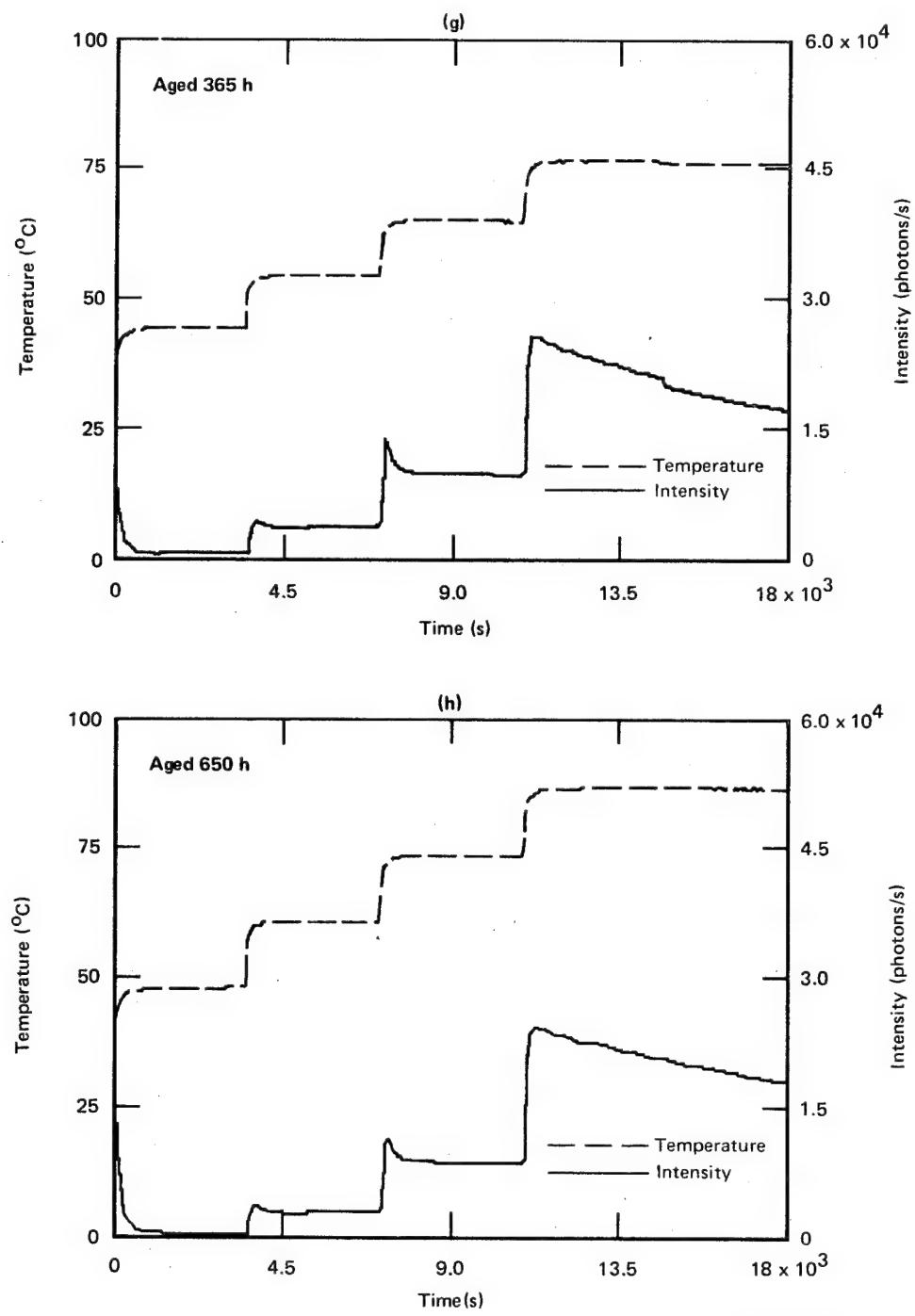
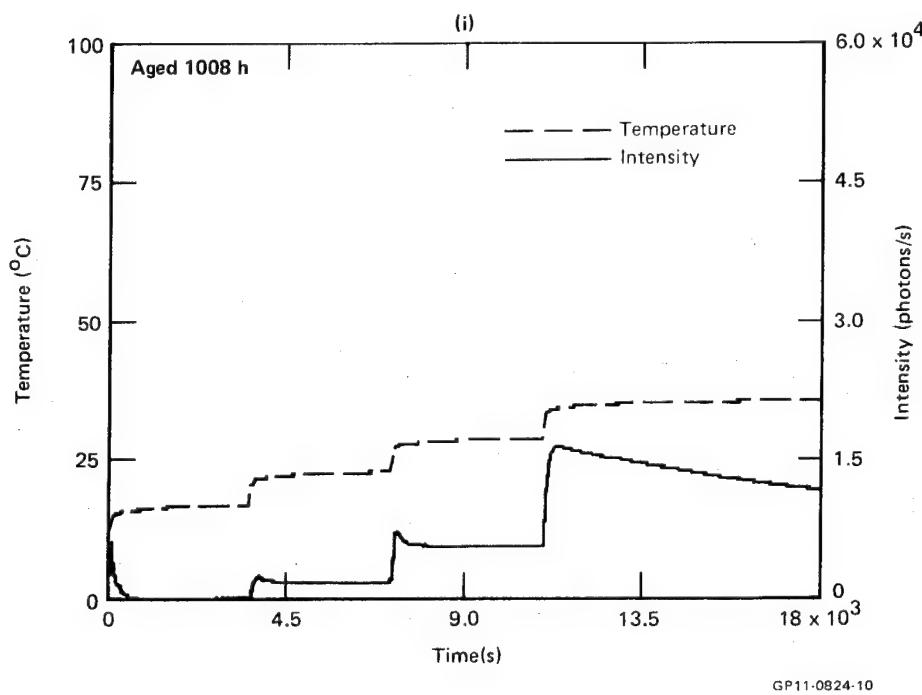
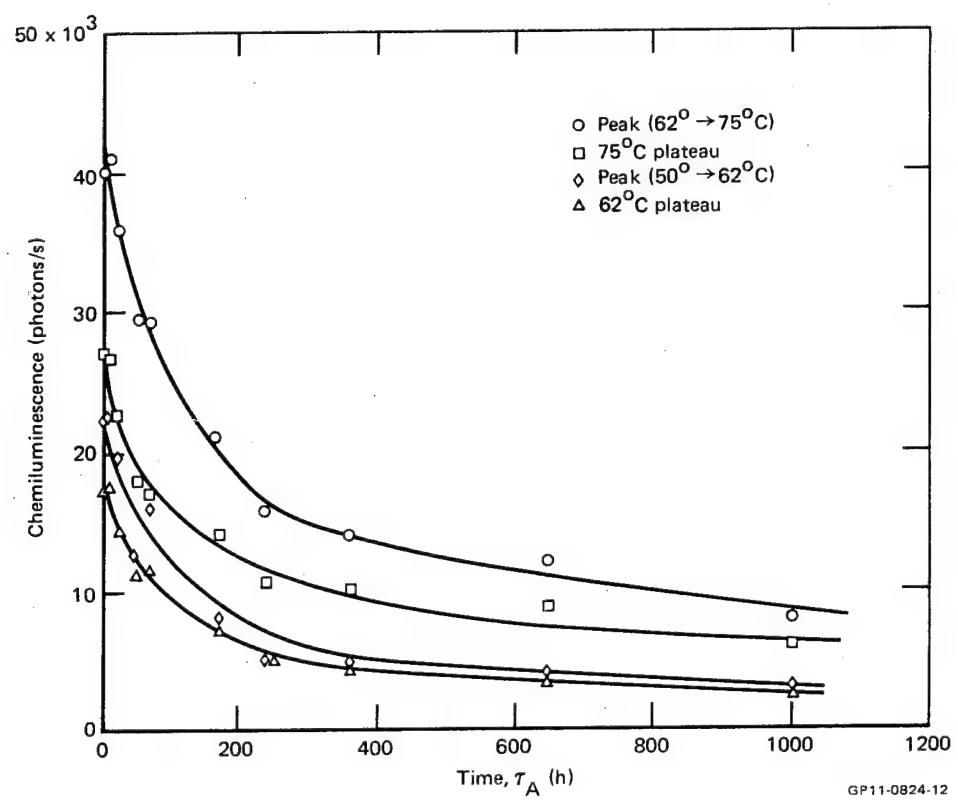


Figure 6 (cont.).



**Figure 6 (concluded).**



**Figure 7. Chemiluminescence at  $75^{\circ}\text{C}$  and  $62^{\circ}\text{C}$  as a function of aging time ( $\tau_A$ ) at  $85^{\circ}\text{C}$  and 50% RH in the absence of mechanical stress.**

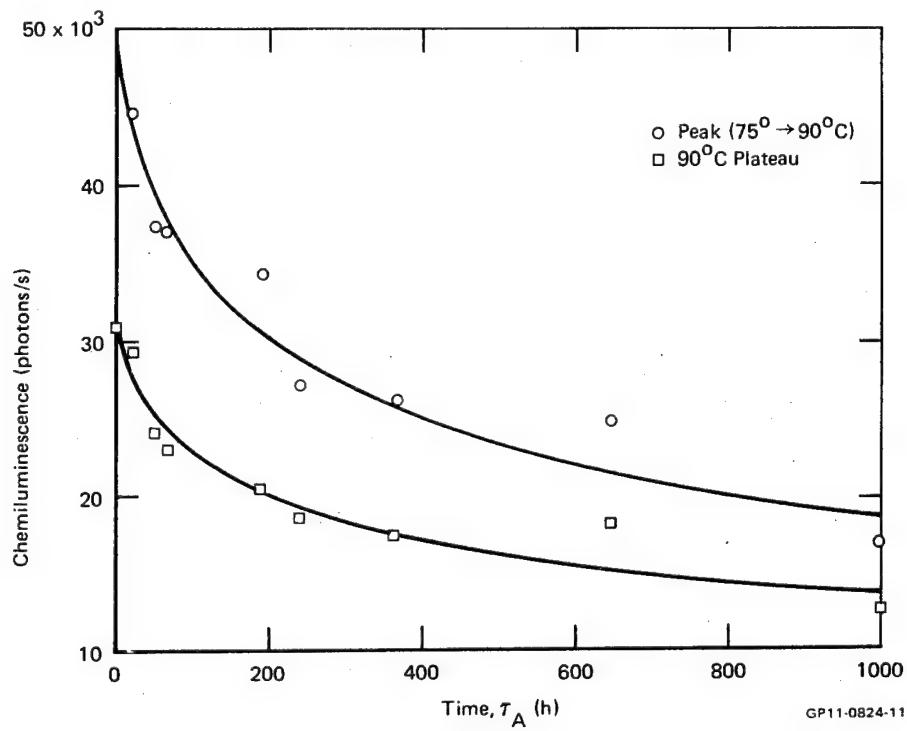


Figure 8. Chemiluminescence at 90°C as a function of aging time at 85°C and 50% RH in the absence of mechanical stress.

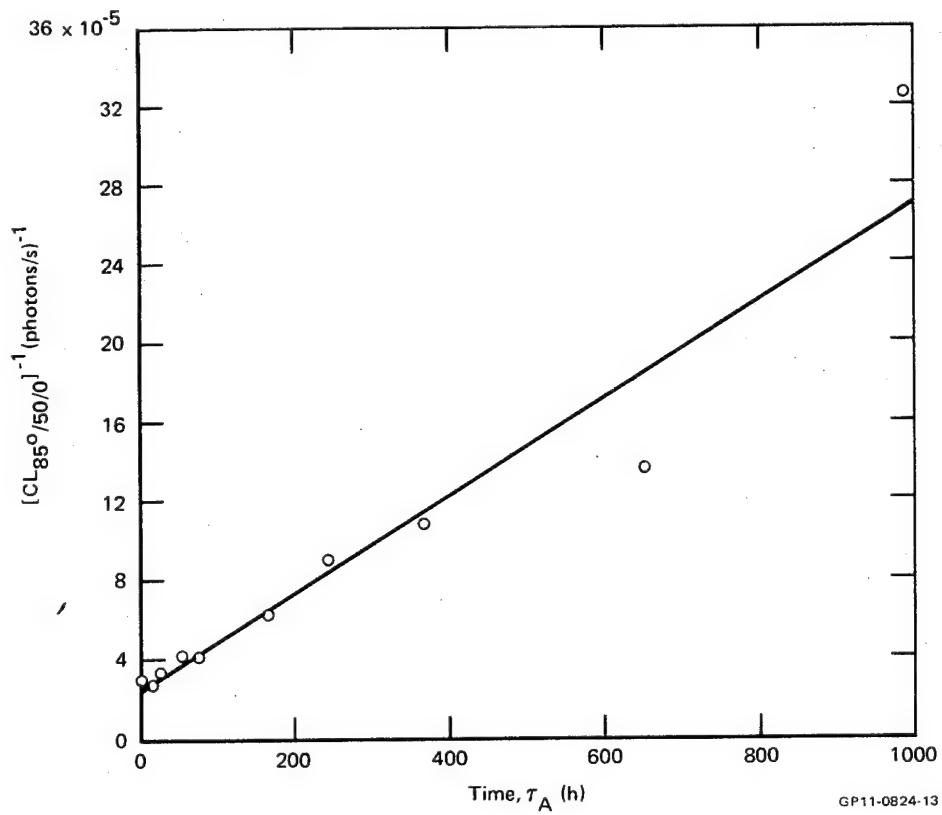
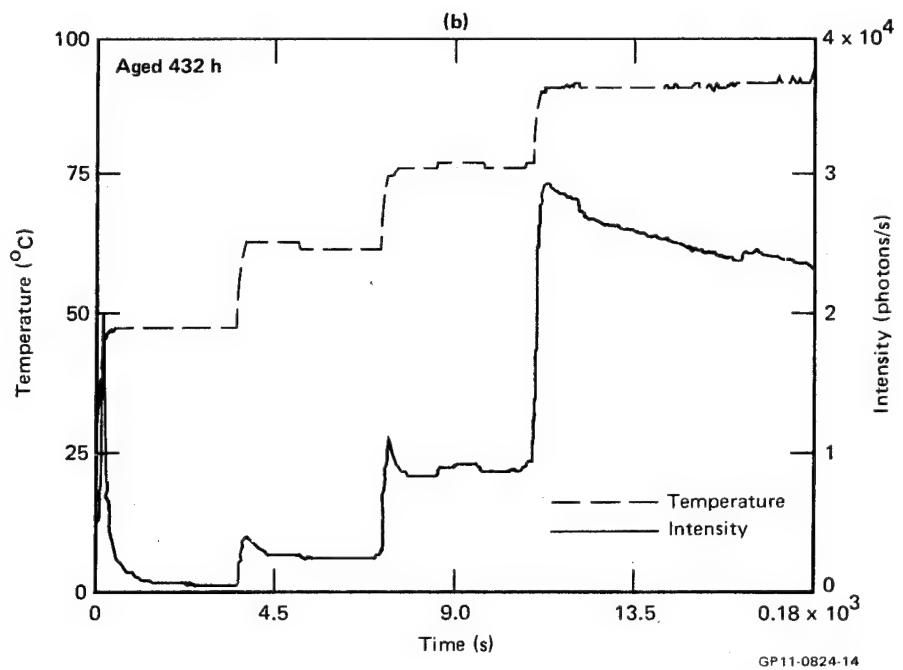
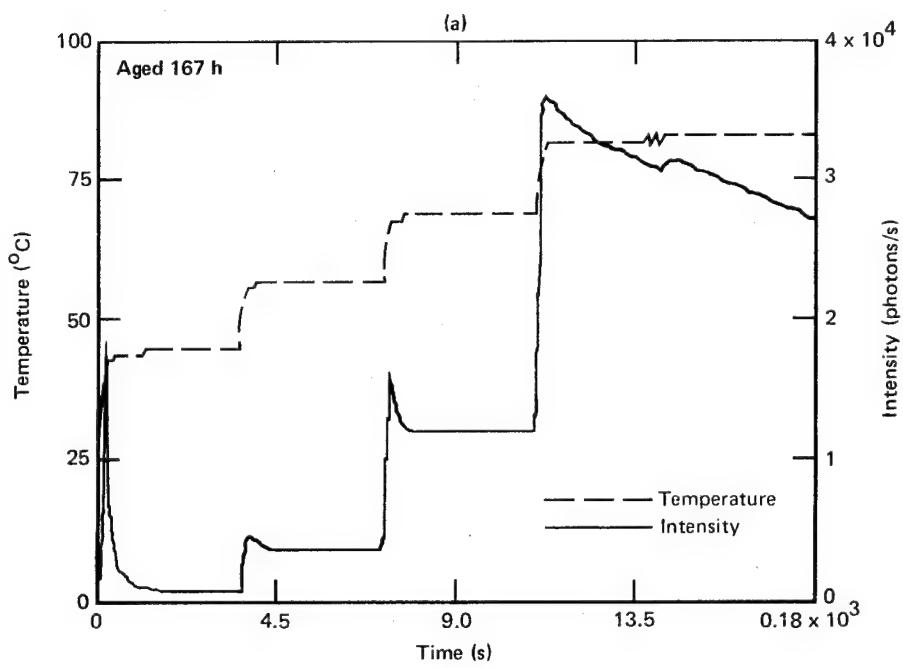


Figure 9. Reciprocal of the chemiluminescence peak (corresponding to the 60°C to 70°C temperature change) as a function of aging time at 85°C and 50% RH in the absence of mechanical stress.



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**Figure 10. Chemiluminescence intensity-temperature-time profiles of the resin aged at 85°C in a dry atmosphere while stressed to 50% UTS.**

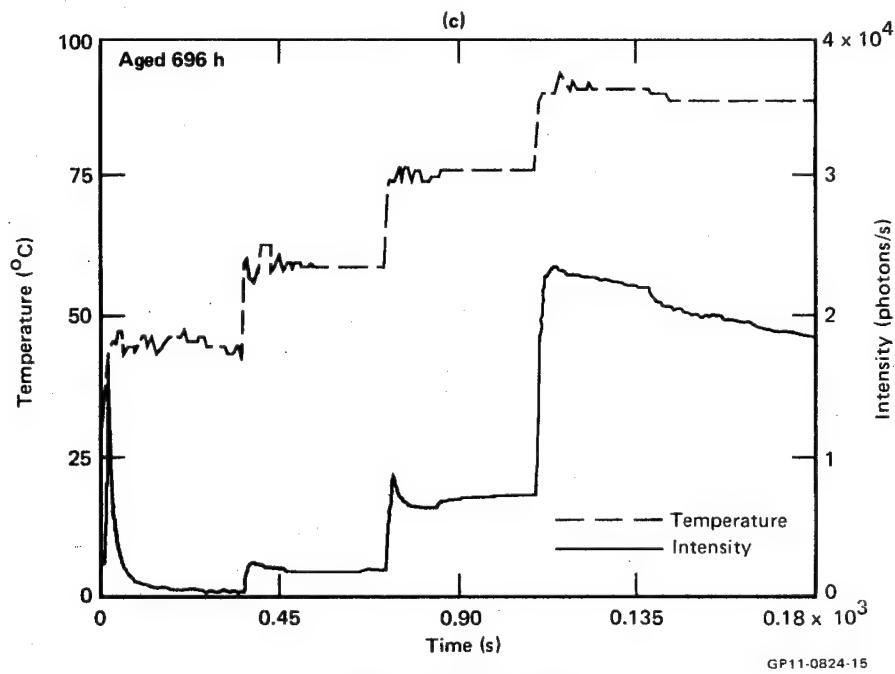


Figure 10 (concluded)

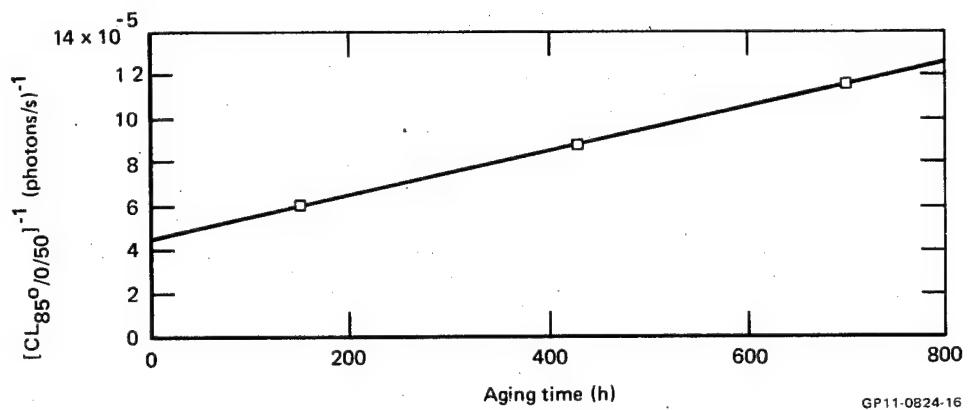


Figure 11. Reciprocal of the chemiluminescence peak (corresponding to the 60°C to 70°C temperature change) as a function of aging time at 85°C in a dry environment while subjected to 50% UTS.

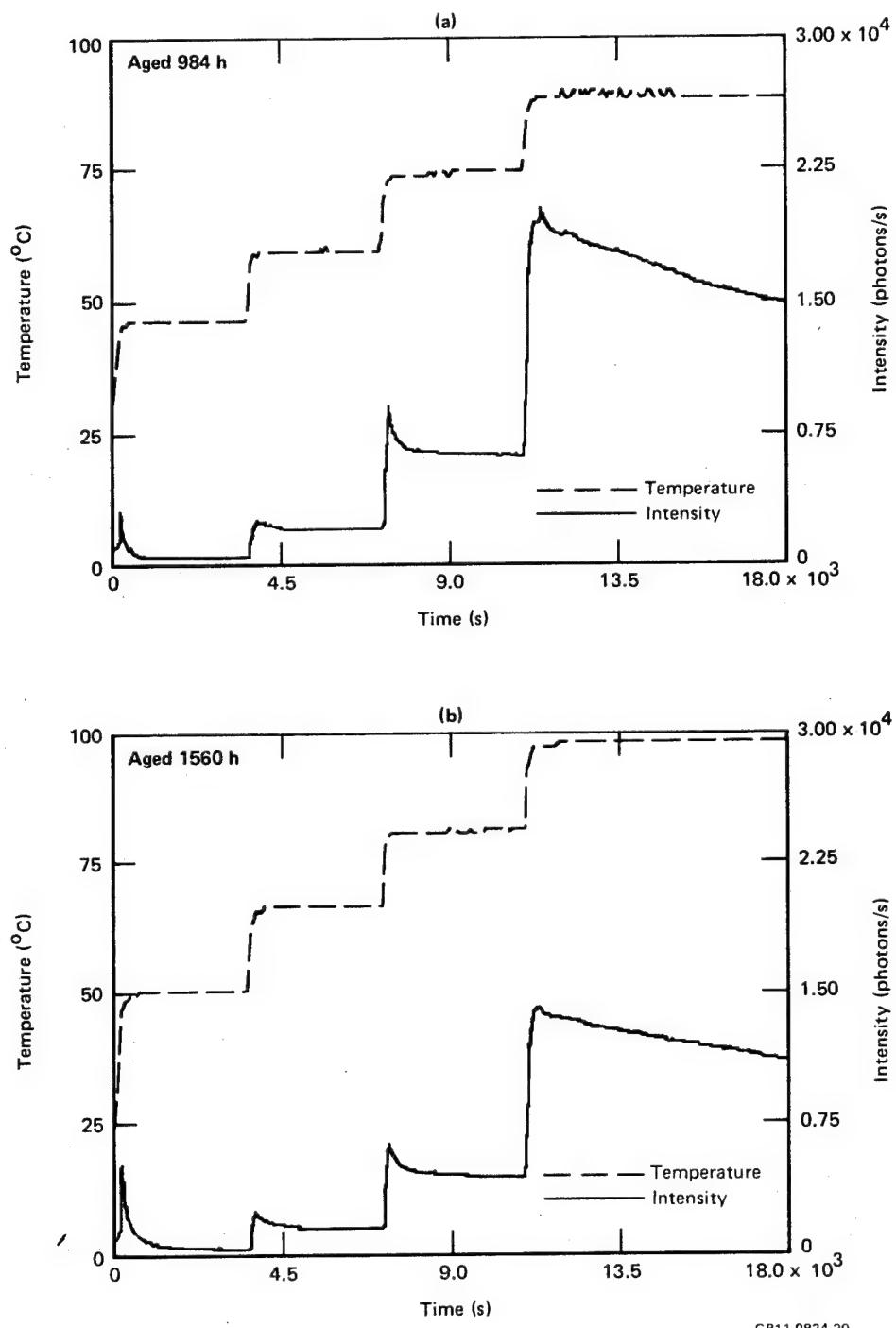
The ITt profiles from the resin aged at 85°C in a moist air atmosphere (50% RH) while subjected to an external tensile stress of 50% UTS are shown in Figure 12. The profiles from aging periods of 984, 1560, and 4704 h are shown in Figures 12(a-c), respectively. A plot of the reciprocal of the intensity from the peak corresponding to the 62° to 75°C thermal transitions is a linear function of the aging period (see Figure 13). The least-squares fit to the experimental data is given by the equation

$$[\text{CL}^{-1}]_{85^\circ, 50, 50} = 1.14 \times 10^{-7} \tau_A - 1.21 \times 10^{-5}. \quad (3)$$

The ITt profiles for the resin aged for 184, 406, 696, and 1152 h at 85°C in a dry air atmosphere (less than 2% RH) and in the absence of external stress are shown in Figures 14(a-d), respectively. Again, the reciprocal of the CL peak intensity from the 60° to 75°C temperature change is a linear function of aging time (see Figure 15) and is given by the equation

$$[\text{CL}]_{85, 0, 0}^{-1} = 0.54 \times 10^{-7} \tau_A + 4.98 \times 10^{-5}. \quad (4)$$

The data summarizing the linear relationship between the reciprocal of the CL peak intensity and the aging time are given in Table 2 where the slope of the line is given for each of the environmental aging conditions investigated. The samples, exposed to the dry environment, exhibit considerably smaller slopes than those exposed to a humid environment. The reason(s) for this difference is not known, but it may result from one of two factors: (1) wet samples age faster and undergo more bond cleavage, or (2) oxygen is more soluble in the wet resin, thereby increasing the rate of chemiluminescence.



**Figure 12. Chemiluminescence intensity-temperature-time profiles of the resin as a function of aging time at 85°C and 50% RH while mechanically stressed to 50% UTS.**

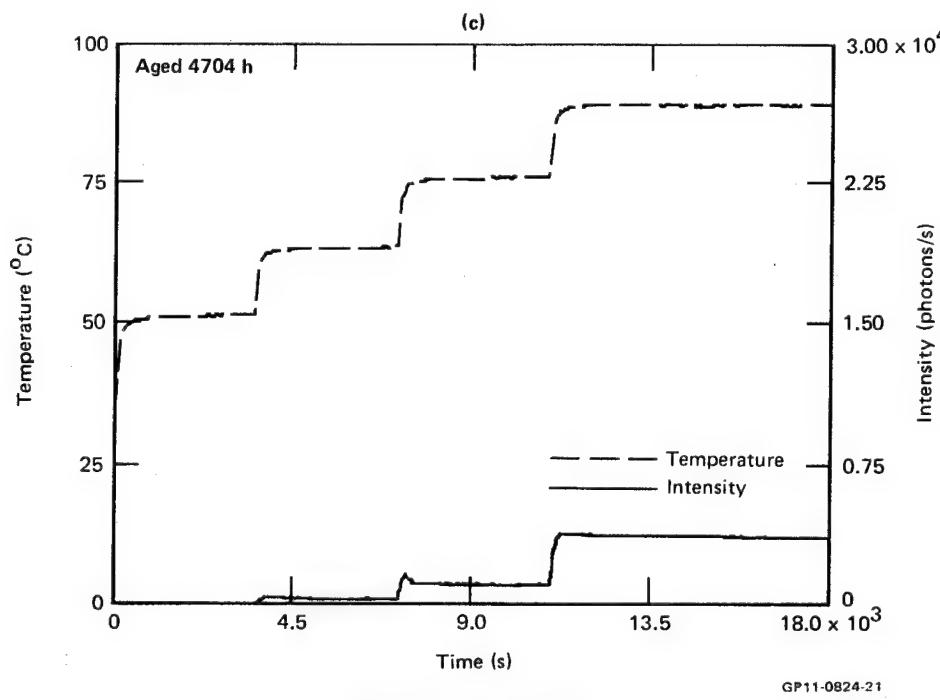


Figure 12 (concluded)

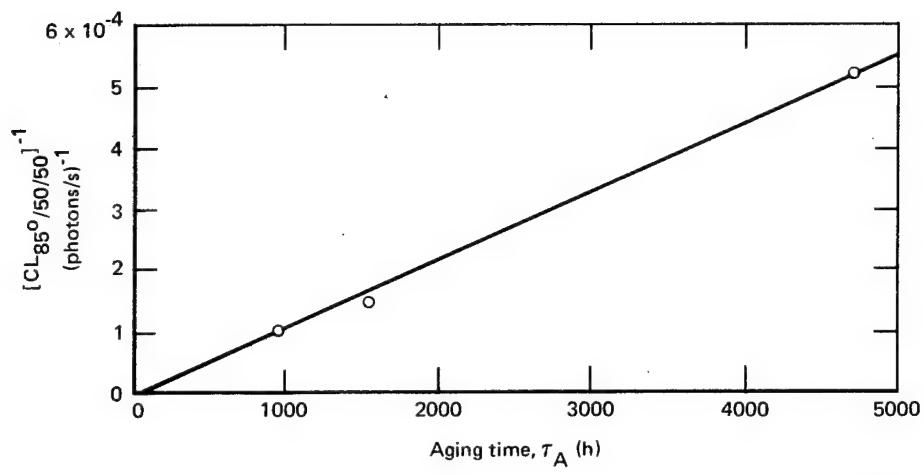
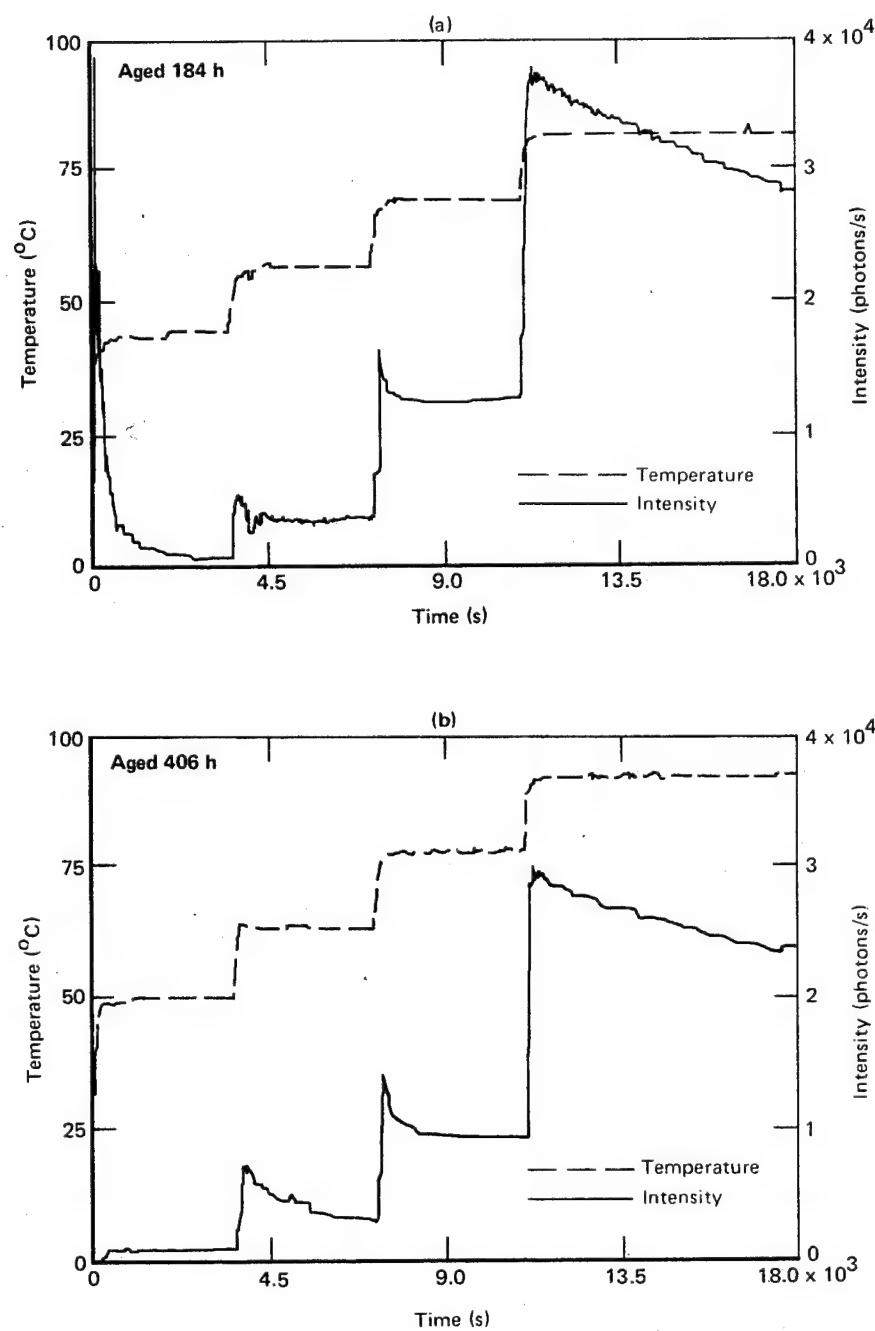
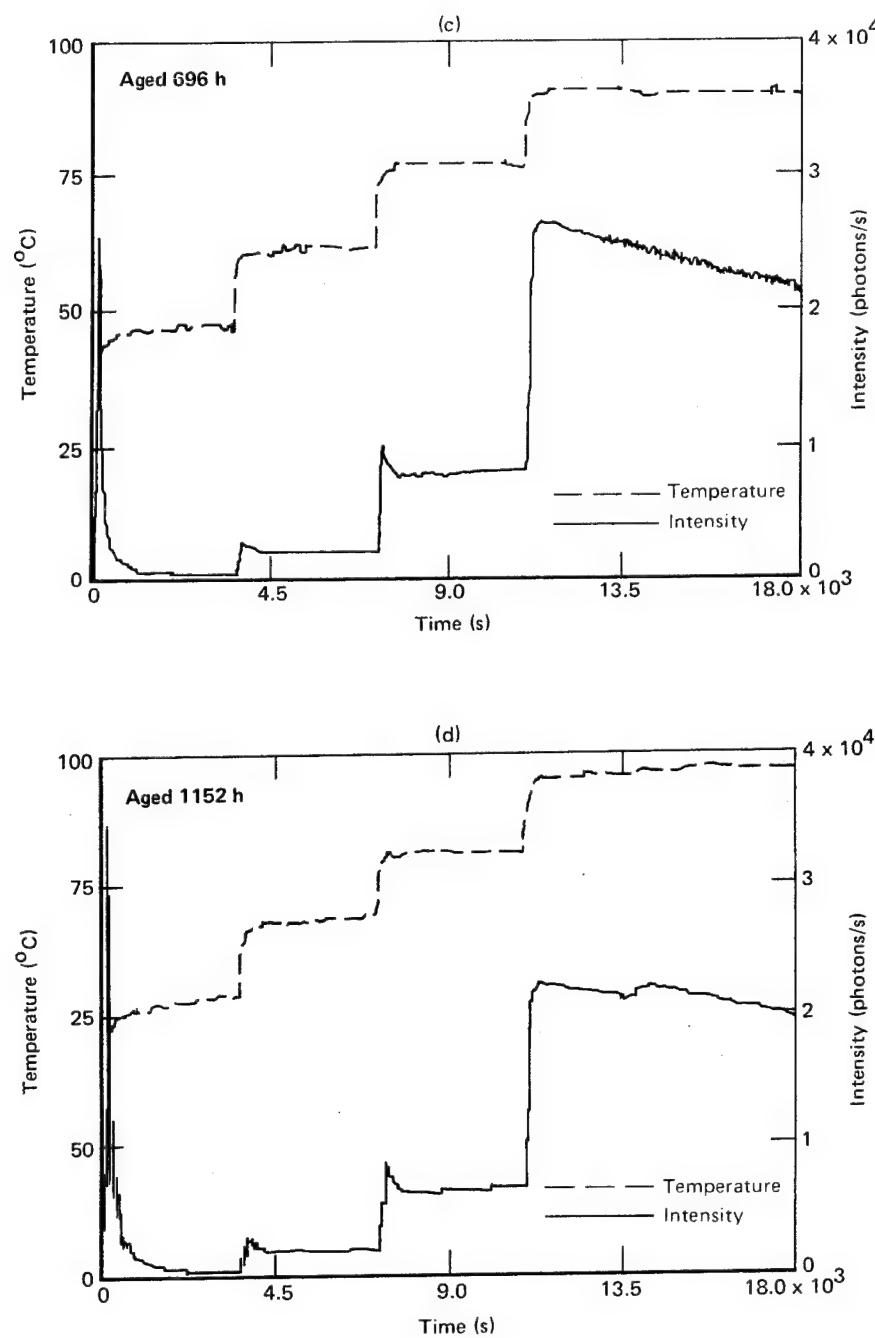


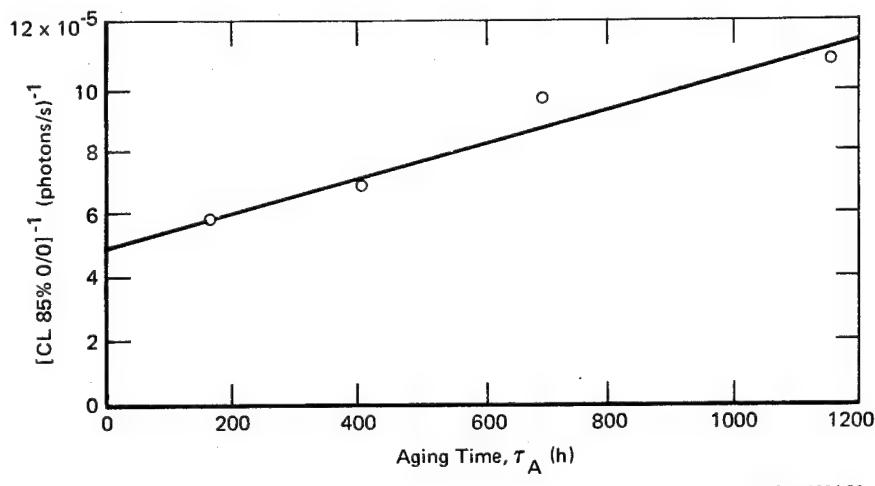
Figure 13. Reciprocal of the chemiluminescence peak (corresponding to the 60° to 70°C temperature change) as a function of aging time at 85°C in a humid atmosphere (50% RH) while subjected to 50% UTS.



**Figure 14.** Chemiluminescence intensity-temperature-time profiles of the resin as a function of aging time at 85°C in a dry atmosphere in the absence of mechanical stress.



**Figure 14 (cont.).**



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**Figure 15. Reciprocal of the chemiluminescence peak (corresponding to the 60° to 70°C temperature change) as a function of aging time at 85°C in a (dry) atmosphere (~2% RH) in the absence of external stress.**

**TABLE 2. SUMMARY OF COEFFICIENTS  
RELATING AGING TIME AT 85°C TO  
RECIPROCAL CHEMILUMINESCENCE  
INTENSITY.**

Temp (°C)	Humidity (%)	Stress (UTS) (%)	Coefficient (s/photon-h)
85	0	0	$0.54 \times 10^{-7}$
85	0	50	0.99
85	50	0	2.69
85	50	50	1.14

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The activation energies (actually the temperature coefficients in an Arrhenius plot) for the change in CL intensity accompanying each temperature increase, i.e., the peaks in the ITT profile, were calculated and are summarized in Table 3. The activation energies for the three peaks, corresponding to a temperature change from 50° to 65°C ( $\Delta E_{50-65}^o$ ), from 65° to 75°C ( $\Delta E_{65-75}^o$ ), and from 75° to 90°C ( $\Delta E_{75-90}^o$ ) are given. Although the peak intensity decreases appreciably during the aging process, the activation energies for the production of CL from each thermal transition is essentially unchanged during aging. This result indicates that the mechanism responsible for the production of CL does not change appreciably during aging, which suggests that CL can be used over a broad temperature range to monitor aging.

in the service environment. A summary of the average activation energies and standard deviation ( $1\sigma$ ) for the three CL peaks observed in the resin samples aged at 85°C is given in Table 4.

The ITt profiles from the resin aged at 150°C in the presence and absence of external tensile stress are shown in Figures 16 and 17, respectively. The ITt profiles from coupons aged at 150°C in the absence of stress for 160, 352, 527, and 816 h are shown in Figures 16(a-d), respectively. The ITt profiles from the samples aged while stressed to 50% UTS for 136, 357, 520, 744, and

TABLE 3. ACTIVATION ENERGIES FOR THE PRODUCTION OF CHEMILUMINESCENCE FROM RESIN AGED AT 85°C.

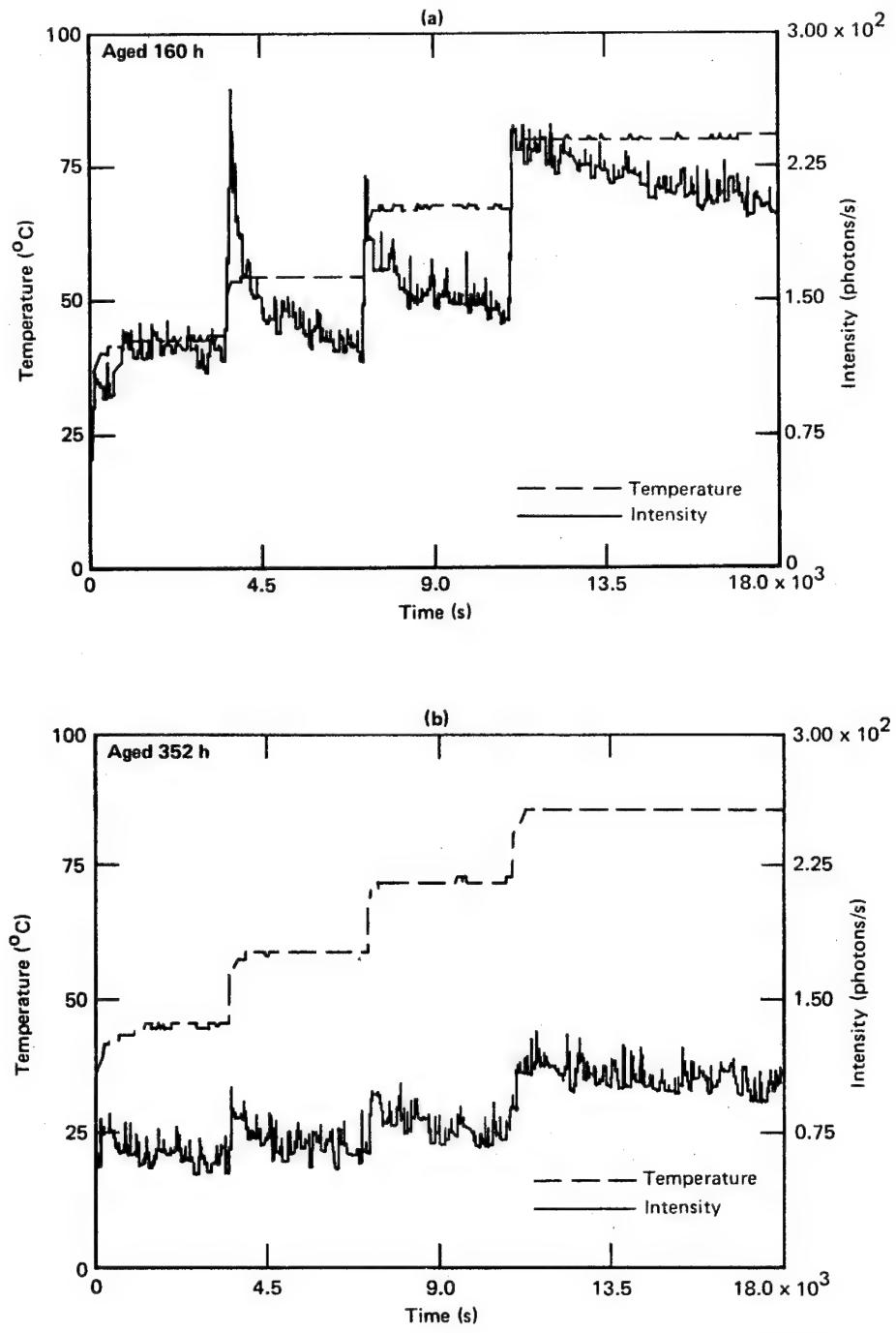
Aging Time (h)	Humidity (%)	Stress (UTS) (%)	$\Delta E_{50-65^\circ}$ (kJ/mole)	$\Delta E_{60-75^\circ}$ (kJ/mole)	$\Delta E_{75-90^\circ}$ (kJ/mole)
184	0	0	135	123	89
406	0	0	121	109	86
696	0	0	112	109	84
1152	0	0	121	114	91
167	0	50	133	133	84
432	0	50	110	107	89
696	0	50	110	98	79
5	50	0	95	79	51
21	50	0	96	81	53
505	50	0	103	81	56
68	50	0	103	81	60
168	50	0	109	91	68
240	50	0	109	95	67
650	50	0	126	112	84
1008	50	0	107	89	72
984	50	50	119	102	86
1560	50	50	103	105	77
2448	50	50	100	96	86
4056	50	50	123	119	98

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TABLE 4. AVERAGE ACTIVATION ENERGIES FOR THE PRODUCTION OF CHEMILUMINESCENCE FROM AGED RESIN.

Aging Temp (°C)	Humidity (%)	Stress (UTS) (%)	$\Delta E_{50-65^\circ}$ (kJ/mole)	$\Delta E_{60-75^\circ}$ (kJ/mole)	$\Delta E_{75-90^\circ}$ (kJ/mole)
85	0	0	$122 \pm 10$	$114 \pm 6$	$87 \pm 3$
85	0	50	$117 \pm 12$	$112 \pm 19$	$84 \pm 5$
85	50	0	$105 \pm 10$	$88 \pm 11$	$64 \pm 11$
85	50	50	$112 \pm 11$	$107 \pm 9$	$86 \pm 9$

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**Figure 16.** Chemiluminescence-temperature-time profiles as a function of aging time at 150°C in the absence of mechanical stress.

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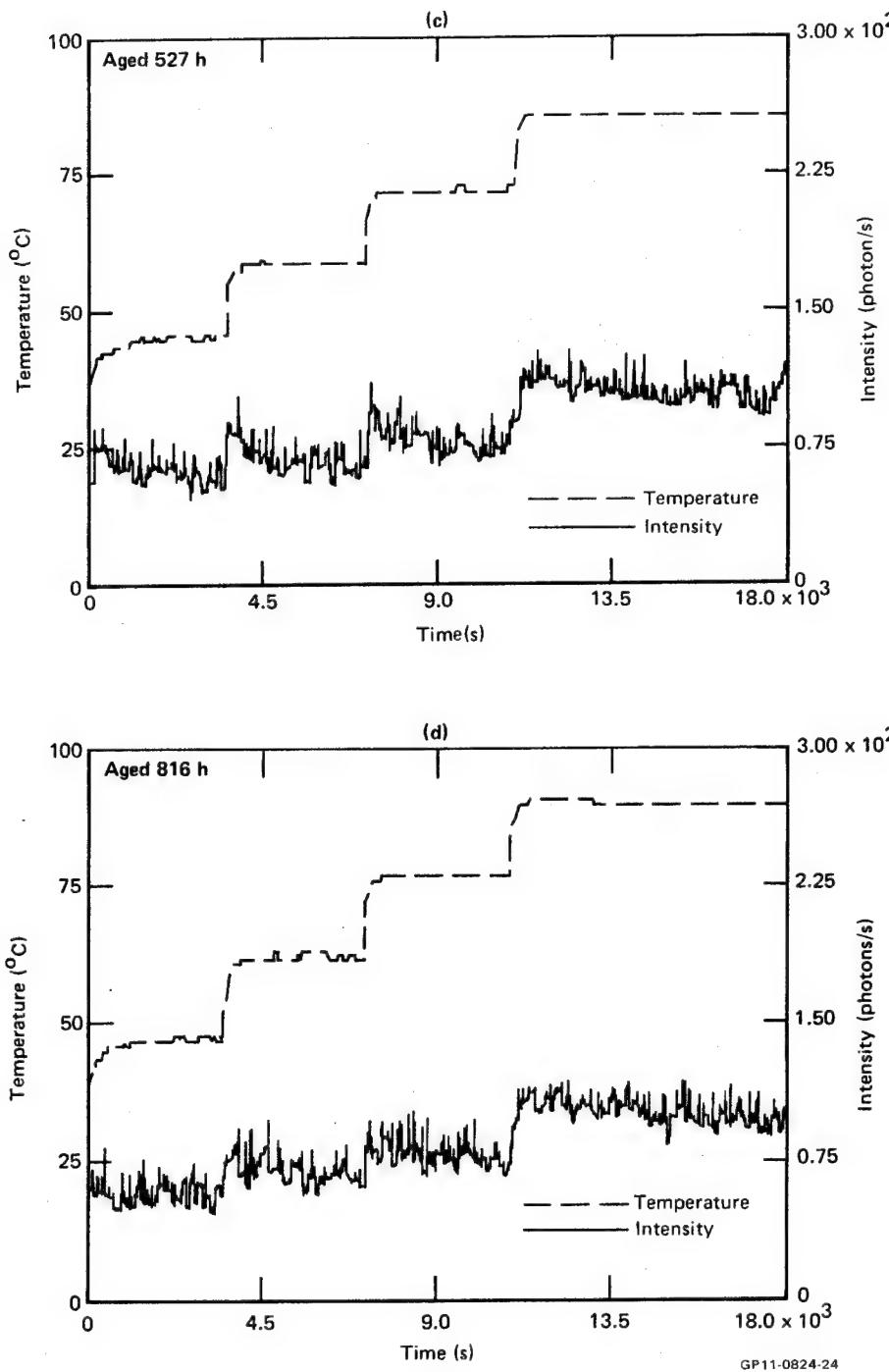
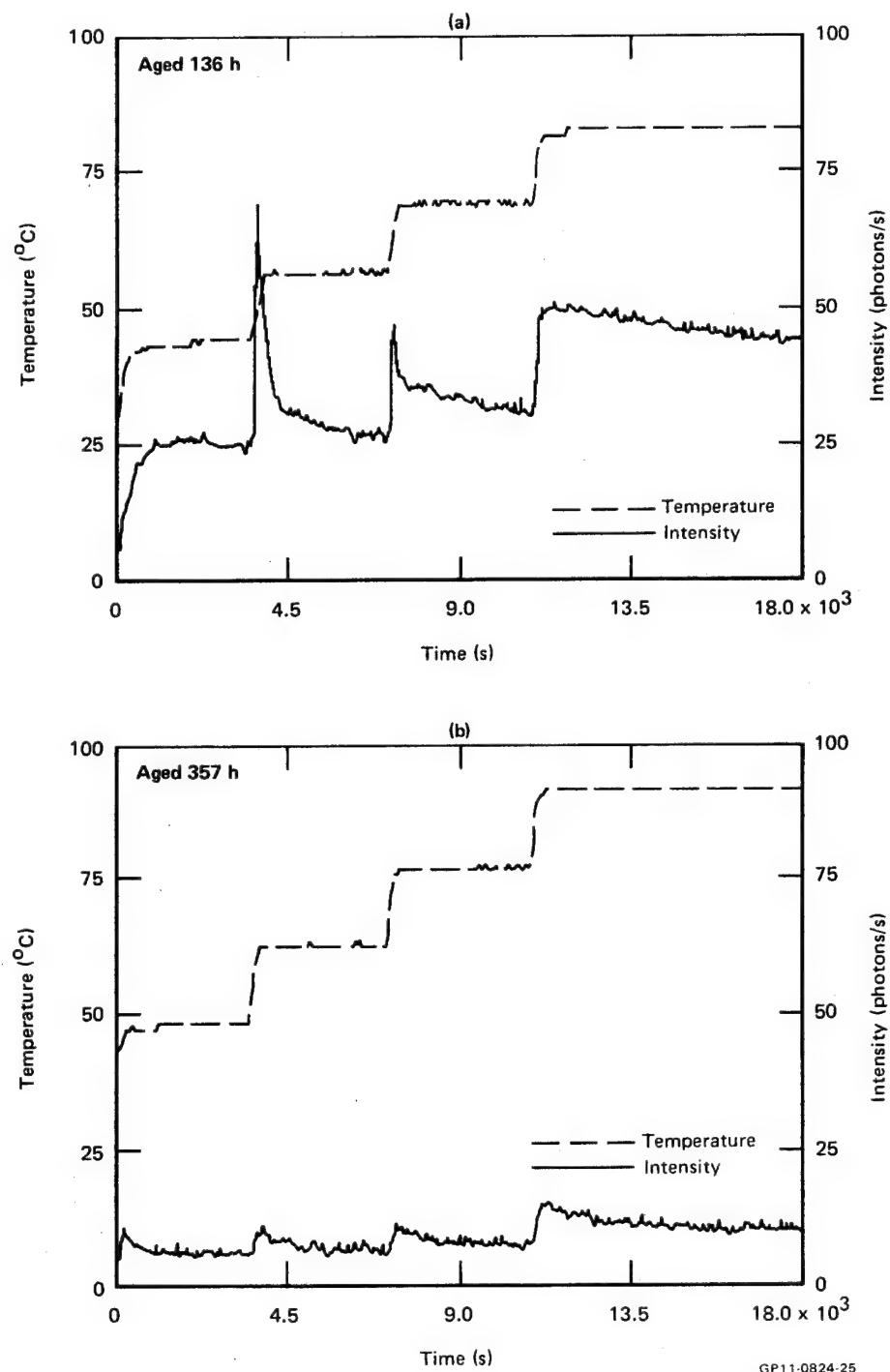


Figure 16 (concluded).



**Figure 17. Chemiluminescence intensity-temperature-time profiles of the resin as a function of aging time at 150°C while stressed to 50% UTS.**

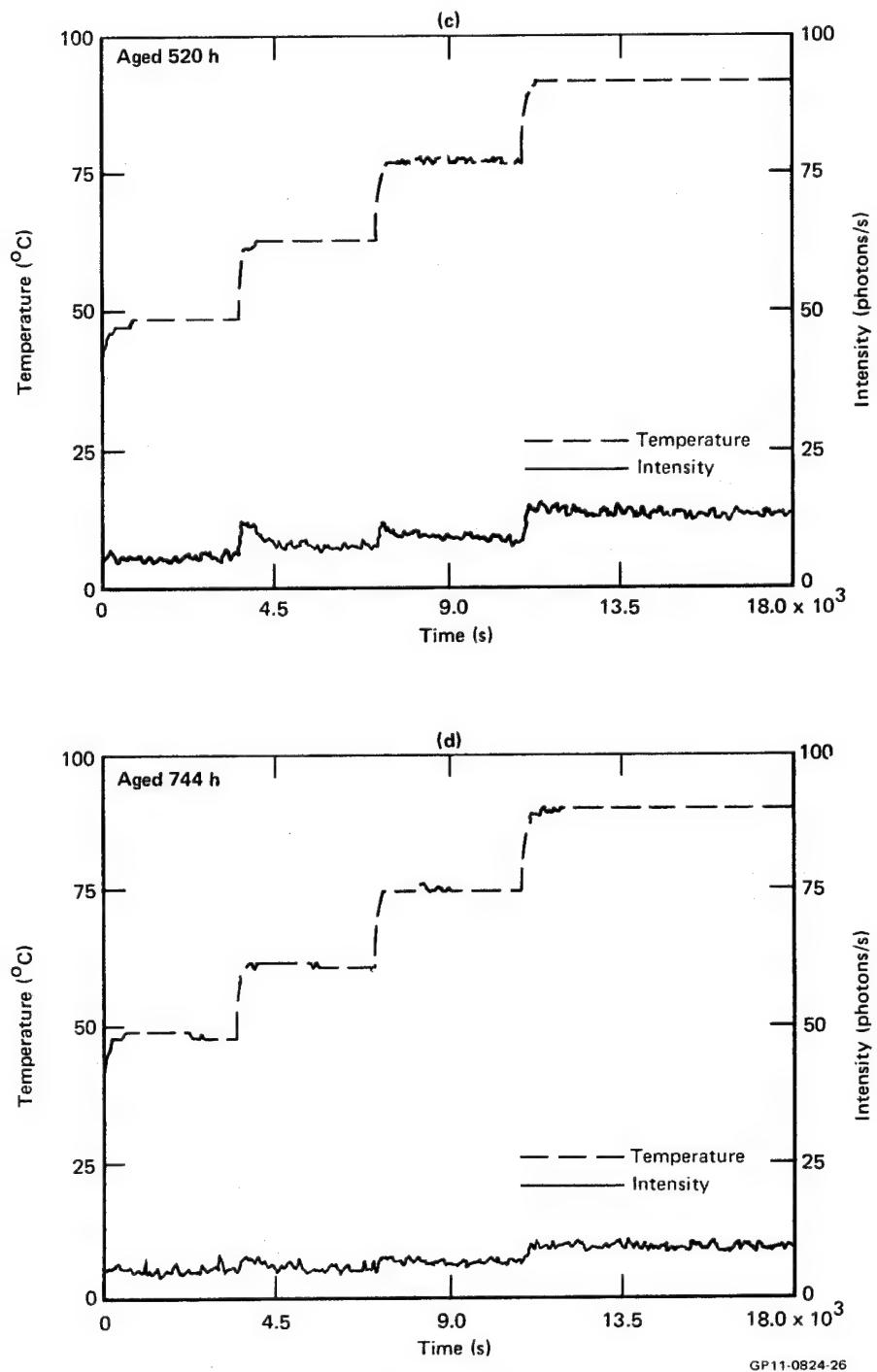


Figure 17 (cont.).

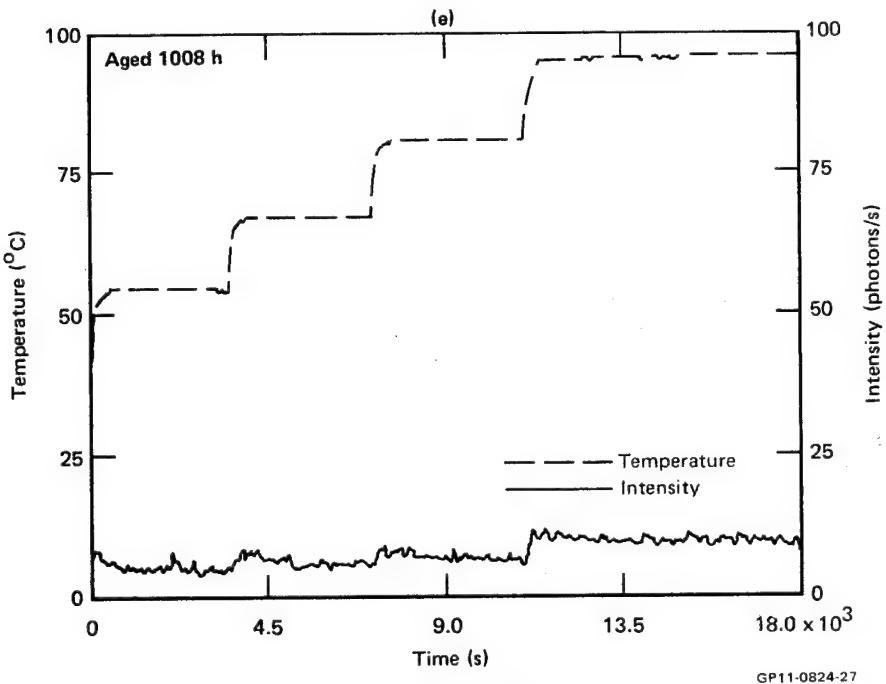


Figure 17 (concluded).

1008 h are shown in Figures 17(a-e), respectively. The CL from samples aged at 150°C, even for relatively short periods of time such as 130-160 h, is reduced markedly from that of samples aged at lower temperatures. The overall CL intensity at any point in the ITt profile is approximately 2 orders-of-magnitude less than that observed in ambient aged coupons. The general form of the ITt profile is different from that observed from samples aged at lower temperatures. The maximum CL peak intensity occurs at the 50-60°C thermal transition, and CL does not increase with temperature. After aging for 200-300 h, the CL intensity is essentially equal to that of the background.

In addition to major changes in CL, the mechanical properties of the resin aged at 150°C are reduced significantly. Three of the samples aged at 50% UTS for > 500 h [Figures 17(c-e)] broke while in the environmental oven. All of the samples, even those stored for 130 h, were markedly darker than the unaged samples. Aging at 150°C drastically changed the chemical and physical properties of the resin even though the samples were post cured at 177°C for 5 h.

#### 4.2 Vaporization Gas Chromatography and Mass Spectrometry of Aged Resin

The volatile low-molecular-weight compounds indigenous to the cured resin were determined by Vap GC. All samples were ground to uniform size prior to analysis to minimize differences resulting from inhomogeneities in particle size distribution. The compounds released following a controlled heating were separated by gas chromatography. A single sample was sequentially heated at the same temperature to yield a series of chromatograms indicating both the composition and quantity of volatile compounds released.

The series of Vap GC chromatograms from 60 mg of unaged, freshly cured resin is shown in Figure 18. Ethanal, propanal, isobutyraldehyde, propenal, butenal, methyl ethyl ketone (MEK), and methyl pentenal were positively identified by mass spectrometry. With the exception of MEK, all compounds

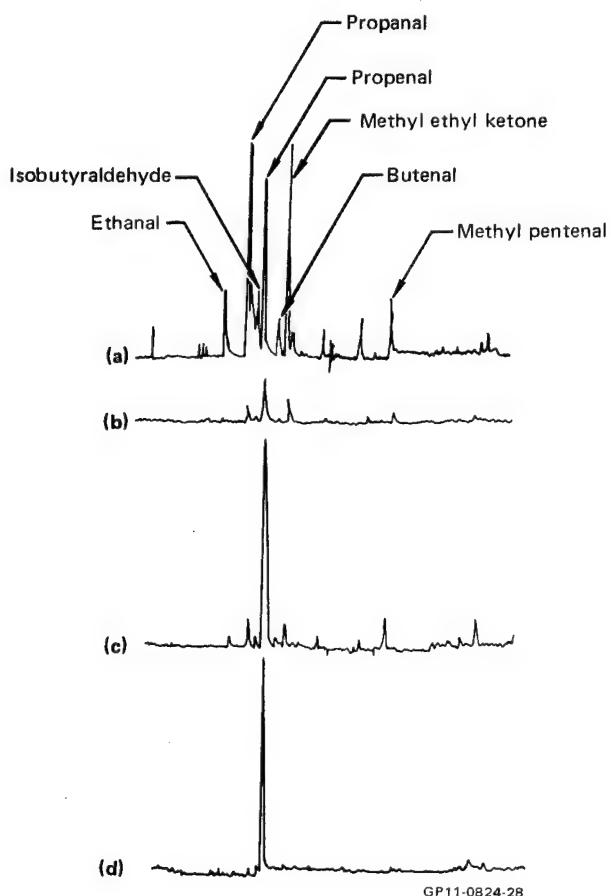


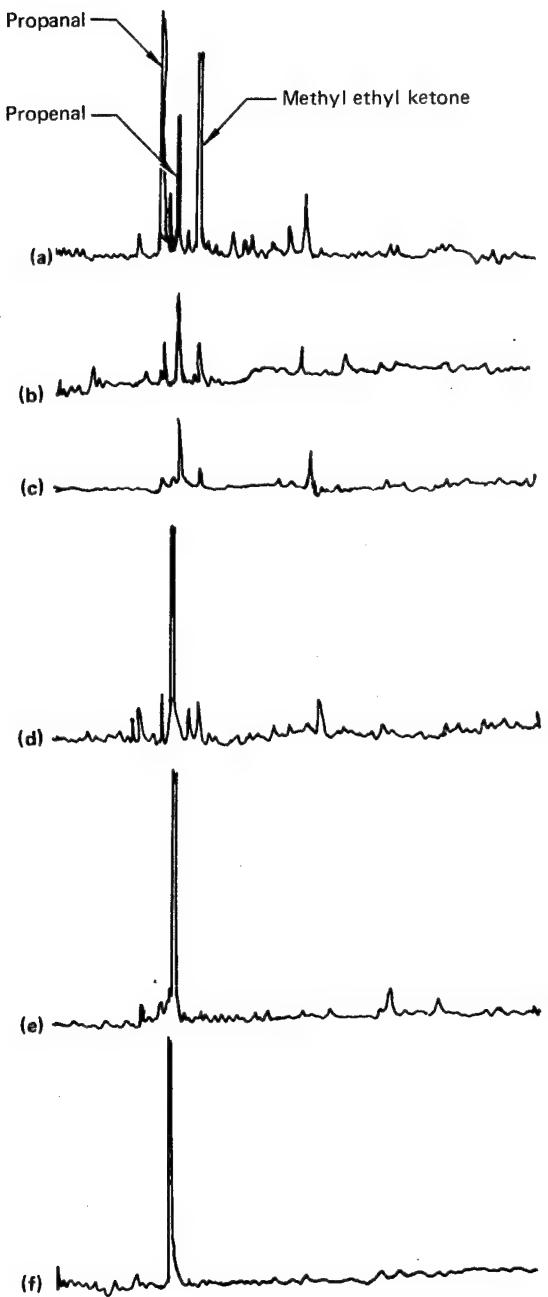
Figure 18. Vaporization gas chromatograms of the compounds released from the virgin resin successively heated for (a) 20 min at 125°C, (b) a second heating at 125°C, (c) 20 min at 175°C, and (d) a second heating at 175°C.

identified (the major products) were aldehydes. Methyl ethyl ketone, an impurity in MY720, remains even after cure. The aldehydes, however, are not major impurities in either the MY720 or DDS and represent compounds characteristic of the resin. These compounds probably are produced during the cure process.

The chromatogram of the compounds released when the unaged resin was heated 20 min at 125°C is shown in Figure 18a. The chromatogram from the second heating is shown in Figure 18b. The total quantity of material released from the second heating is an order-of-magnitude less than that from the first. The resin then was heated to 175°C for 20 min, and the chromatogram of the products is shown in Figure 18c; the chromatogram of the compounds collected from a second 20 min heating at 175°C is shown in Figure 18d. The large increase in the amount of propenal observed from the resin heated at 175°C compared to that observed from the second heating at 125°C suggests that propenal is produced at 175°C.

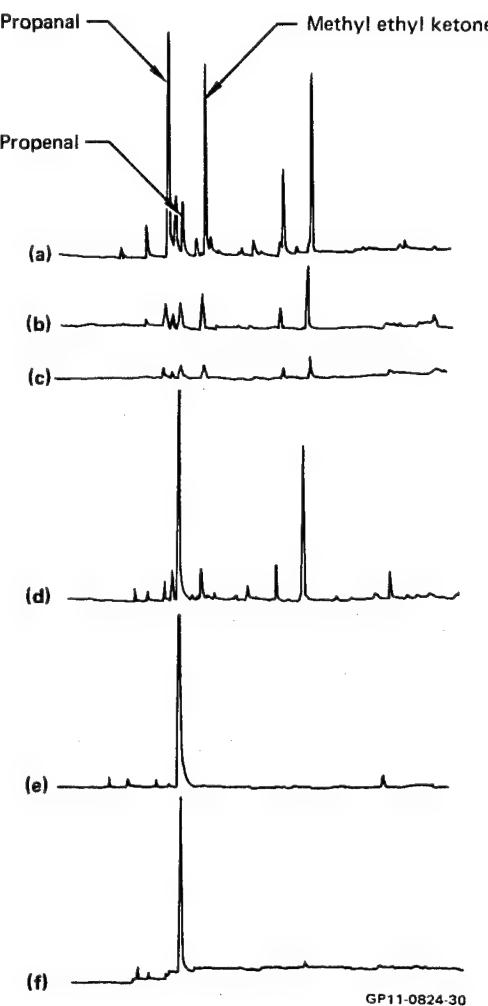
The Vap GC chromatograms from a typical sample of resin aged for 1176 h (49 days) at 85°C in a dry atmosphere while stressed to 50% UTS is shown in Figure 19. The major products are propanal (a), propenal (b), MEK (c), and methyl pentenal (d). The chromatogram of the compounds released when the sample was first heated at 125°C, when heated for the second time at 125°C, and the third time at 125°C are shown in Figures 19(a-c), respectively. The chromatograms of the products released when the same sample was heated for a series of three 20-min heatings at 175°C are shown as Figures 19(d-f), respectively.

The Vap GC chromatograms from a typical resin aged for 169 h at 85°C in a moist atmosphere (50% RH) but unstressed are shown in Figure 20. The compounds identified include propanal (a), propenal (b), MEK (c), and methyl pentenal (d). The chromatogram of the compounds released from the first heating at 125°C, the second heating at 125°C, and the third heating at 125°C are shown in Figures 20(a-c), respectively. The chromatogram of the products released from the first heating at 175°C, the second heating at 175°C, and the third heating at 175°C are shown in Figures 20(d-f), respectively.



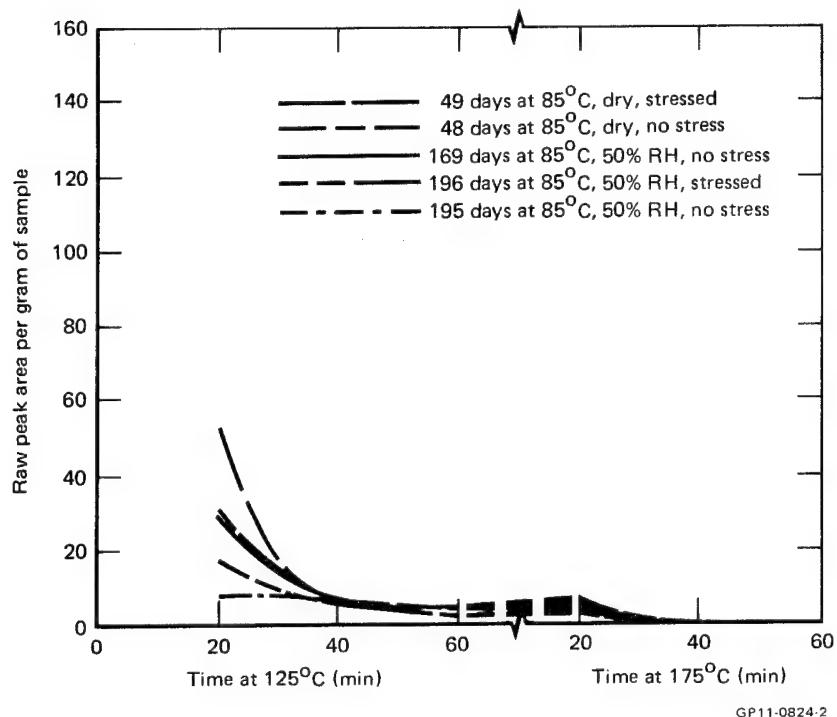
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**Figure 19.** Vaporization gas chromatograms of the compounds released from the resin aged for 48 days at 85°C in a dry atmosphere in the absence of external stress. The sample was successively heated for (a) 20 min at 125°C, (b) a second heating at 125°C, (c) a third heating at 125°C, (d) 20 min at 175°C, (e) a second heating at 175°C, and (f) a third heating at 175°C for 20 min.

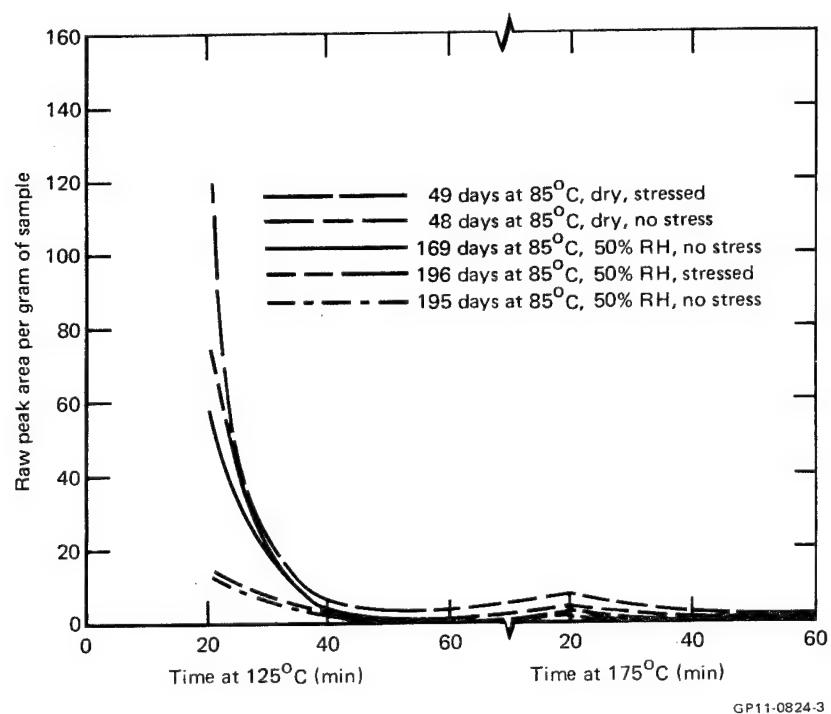


**Figure 20.** Vaporization gas chromatograms of the compounds released from the resin aged for 169 days at 85°C in a humid atmosphere (50% RH) in the absence of external stress. The sample was successively heated for (a) 20 min at 125°C, (b) a second heating for 125°C at 20 min, (c) a third heating for 20 min at 125°C, (d) 20 min at 175°C, (e) a second heating for 20 min at 175°C, and (f) a third heating for 20 min. at 175°C.

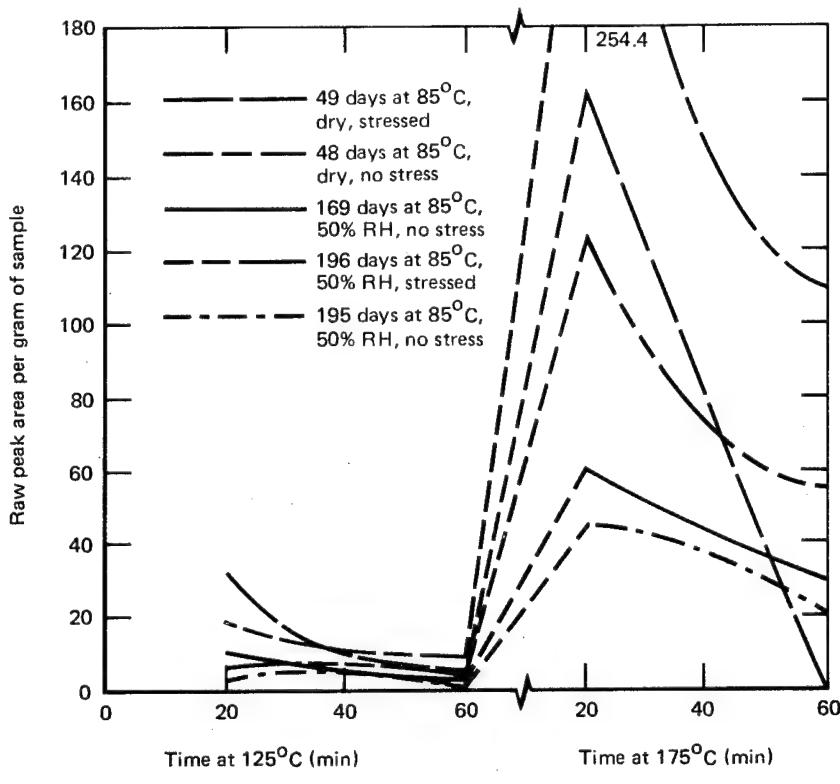
An analysis of the Vap GC data from a series of resin samples aged at 85°C in the presence and absence of moisture and/or external tensile stress shows three compounds of particular interest: MEK, propanal, and propenal. The normalized quantities (i.e., the chromatographic peak area divided by the weight of the powdered resin analyzed) of MEK, propanal, and propenal released during each of the six heating periods (three at 125°C and three at 175°C) are shown in Figures 21, 22, and 23, respectively. Relatively large quantities of both methyl ethyl ketone and propanal were released during the first heating at 125°C, but little was released during subsequent heating at either 125° or 175°C (see Figures 21 and 22). This result suggests that both of these



**Figure 21. Relative amount of methyl ethyl ketone released from successive heating at 125°C and 175°C for aged resin samples.**



**Figure 22. Relative amount of propanal released from successive heating at 125°C and 175°C for aged resin samples.**



**Figure 23. Relative amount of propenal released from successive heating at 125°C and 175°C for aged resin samples.**

compounds are indigenous volatile materials trapped in the resin matrix at the time of cure. The release of propenal is, however, quite different; the quantity released at 175°C is considerably greater than that released at 125°C for all samples investigated. The most pronounced difference occurred in the resin aged for 48 days in a dry atmosphere in the absence of mechanical stress. However, these apparent differences are not as large as they appear in Figure 23; the ratio of the quantity released at 175°C to that released at 125°C is essentially the same regardless of the aging environment. These ratios together with the calculated temperature coefficients (activation energies) for propenal production from 125° to 175°C are summarized in Table 5. The average value of the ratio of the quantity released at 175°C to that released at 125°C is 25.6, and the corresponding activation energy and its standard deviation ( $1\sigma$ ) is  $96 \pm 4$  kJ/mole. It is not likely that the propenal observed in the Vap GC experiments is the result of residual material trapped in the matrix. Several observations support this hypothesis: 1) little propenal was observed during Vap GC analysis of unpolymerized MY720, 2) the

TABLE 5. ACTIVATION ENERGIES FOR THE RELEASE OF PROPENAL FROM AGED RESIN SAMPLES.

Aging conditions					
Temp (°C)	Humidity (%)	Stress (UTS) (%)	Time (days)	Ratio propenal released at 175°/125°	Δ E (kJ/mole)
85	0	0	48	27.1	98
85	0	50	49	27.3	98
85	50	50	196	26.0	96
85	50	0	169	19.5	88
85	50	0	195	28.3	99
Average				(25.6 ± 3.5)	(96 ± 4)

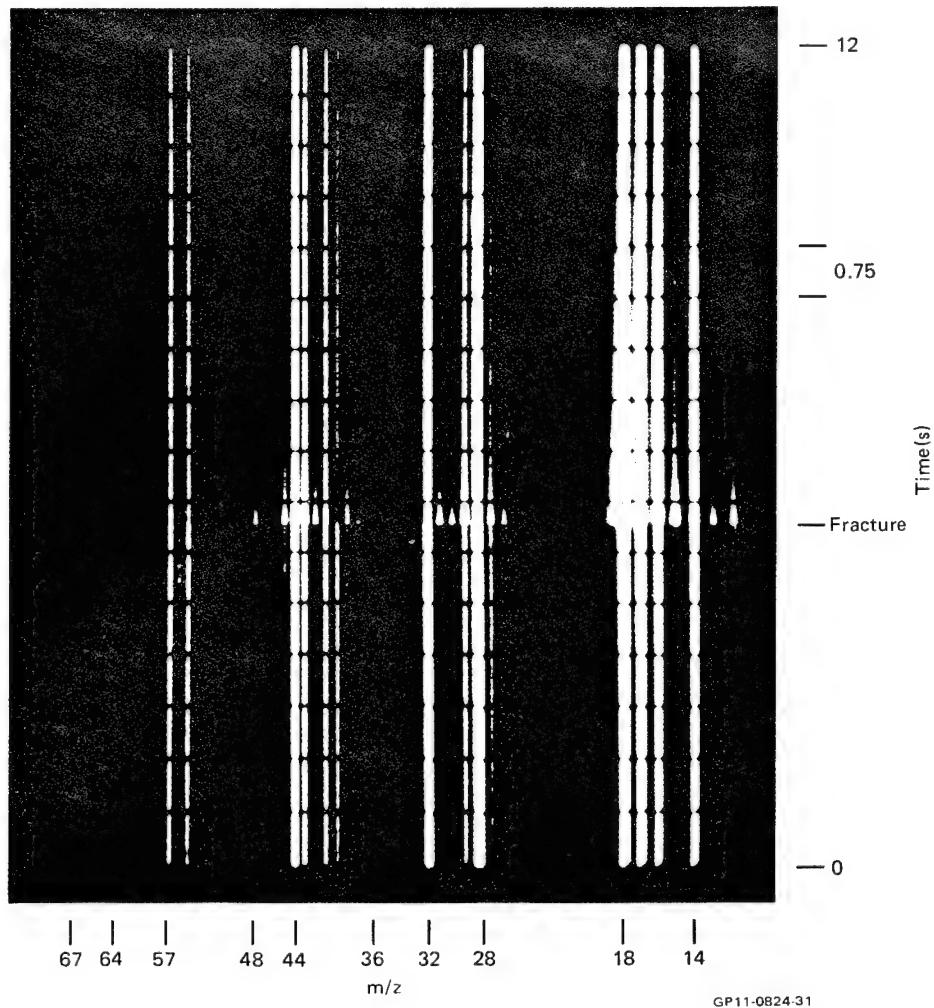
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amount of propenal released at 175°C is 25 times greater than that released at 125°C, and 3) propenal is a relatively reactive, unstable liquid at room temperaure.<sup>24</sup> Propenal can be formed by the decomposition and subsequent rearrangement of an unreacted glycidyl group or by the cyclization of two neighboring glycidyl groups followed by subsequent decomposition.

#### 4.3 Stress Mass Spectrometry

The compounds released upon fracture of the cured resin were investigated by stress MS. When stress MS is coupled with the information available from Vap GC, useful information regarding the generation of mechanochemical products can be obtained. The two methods can be used to distinguish between mechanically generated compounds and residual or thermally generated compounds.

Dogbone-shaped samples of the resin were fractured in the TOFMS, and the mass spectrum of the compounds released was measured. A typical rapid-event mass spectral data analysis display (REMSDA) is shown in Figure 24. The mass-to-charge ratio is displayed along the abscissa, and the time along the ordinate; intensity of the line is proportional to the concentration. The data shown in Figure 24 were obtained from the fracture of an MY720/Eporal resin which had been aged for two months in the ambient environment. The intensity of several ions increases notably upon fracture. The ions with mass-to-charge (m/z) 18 and 17 correspond to H<sub>2</sub>O; they are so intense and omnipresent in these experiments that they are of little analytical value. The ions at m/z 45, 41, 31, 30, 27, and 26 are consistent with the observation



**Figure 24.** Mass spectrum of the compounds released from the fracture of MY720/Eporal resin (REMSDA display).

that several aldehydes are present in the cured resin. The ions at  $m/z$  64 and 48, however, are indicative of  $\text{SO}_2$  which apparently is not indigenous to the resin. The presence of  $\text{SO}_2$  was confirmed by repeating the experiments with a low ionizing potential (11.4 eV) and noting that the fragmentation pattern was that expected from  $\text{SO}_2^+$ .

The stress MS analyses of the resin aged at ambient conditions for several hundred hours at  $85^\circ\text{C}$  and 160 h at  $150^\circ\text{C}$  all showed the presence of  $\text{SO}_2$ ; however, a quantitative estimate of its concentration could not be made.

#### 4.4 Fourier Transform Infrared Spectrometry

The infrared spectra of the cured resin samples were measured as a function of aging by the technique of attenuated total reflectance. A typical spectrum from an unaged sample is shown in Figure 25. The peaks of primary interest, at least with respect to the CL and aging studies, are the carbonyl bands at 1630 and 1720  $\text{cm}^{-1}$ . The peak at 1630  $\text{cm}^{-1}$  probably results from the partial oxidation of the methylene group in the glycidyl moiety to  $>\text{N}-\overset{\text{O}}{\text{C}}-\text{}$ .<sup>28</sup> However, as the samples age, they become increasingly darker, and the depth in which the IR penetrates the resin decreases. Therefore it is difficult to obtain useful data with the ATR method, and conventional transmission IR analysis is even more difficult. Changes in the carbonyl portion of the spectra cannot be obtained readily with the relatively thick samples used for the stress and CL analysis. Therefore, little useful information other than noting the presence of a  $>\text{N}-\overset{\text{O}}{\text{C}}-\text{}$  functional group was obtained.

#### 4.5 Precision Abrasion Mass Spectrometry

The water, oxygen, carbon dioxide, and nitrogen concentrations and their distributions as a function of depth within the resin samples were measured by

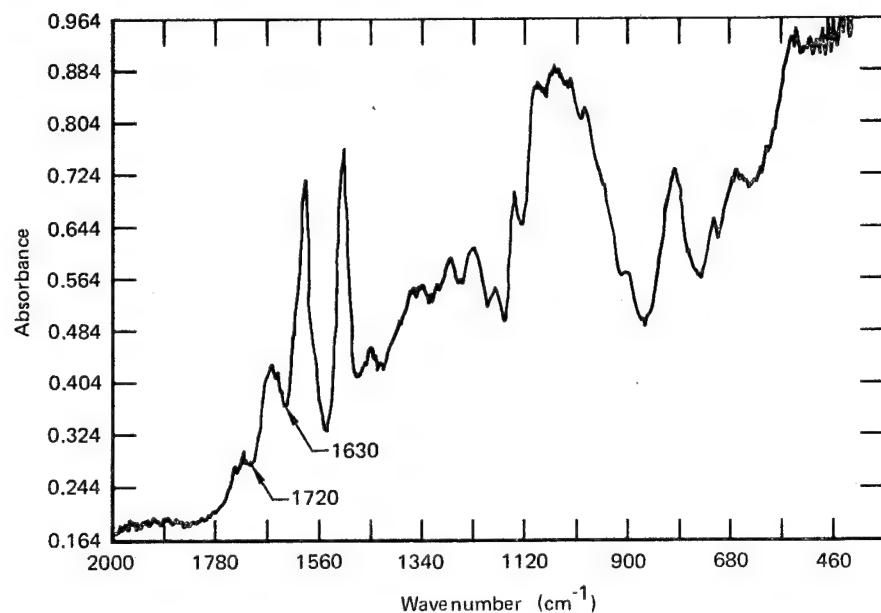
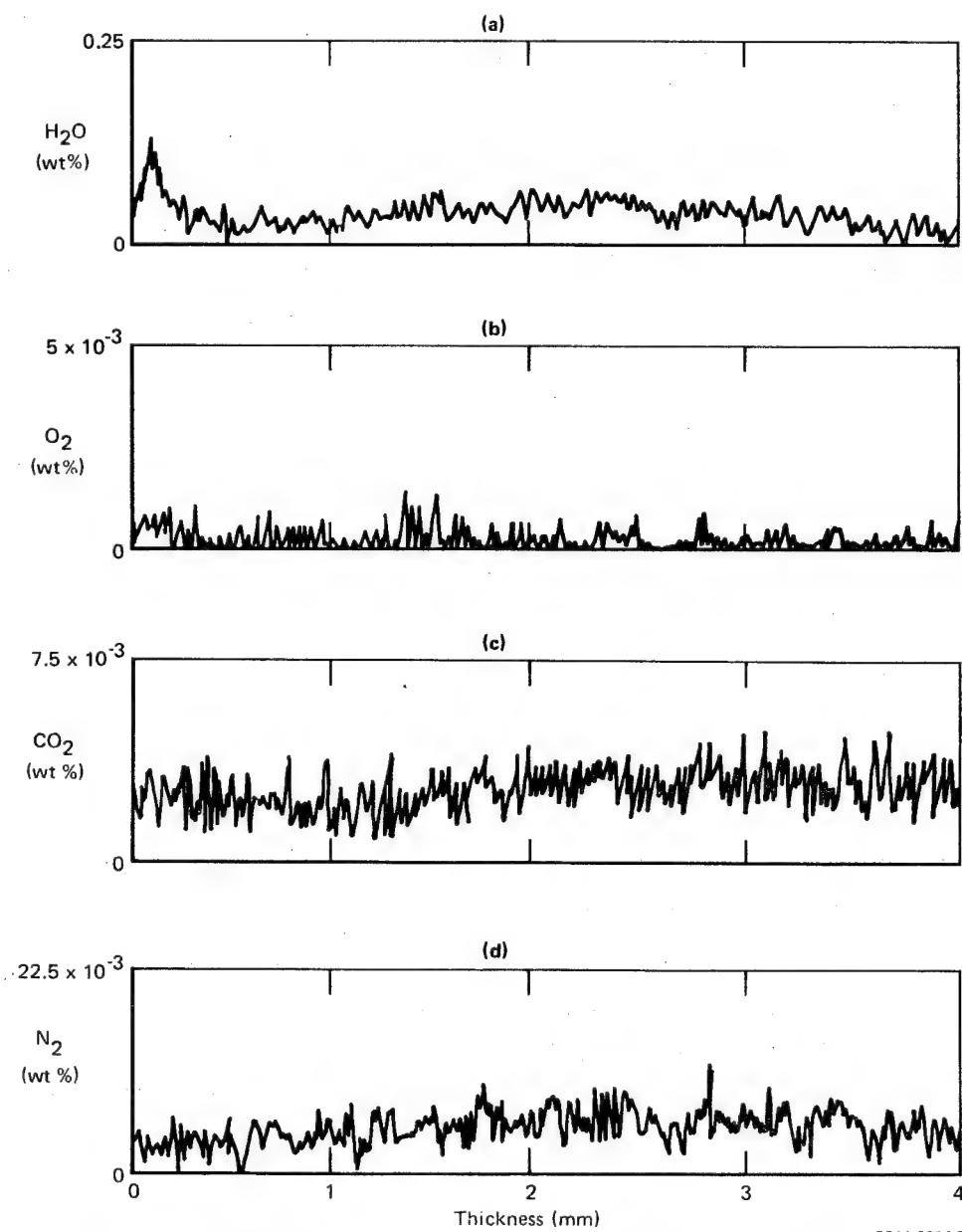


Figure 25. Infrared spectrum (ATR-FTIR) of the resin after exposure to the ambient environment for 1 month.

PAMS. The  $H_2O$  concentration was highest near the surface because water rapidly sorbed from the atmosphere after fabrication. The overall water concentration in the interior of the resin was low, and its concentration varied from 0.05 to 0.1 wt%. Typical distribution curves for  $H_2O$  (a),  $O_2$  (b),  $CO_2$  (c), and  $N_2$  (or  $CO$ ) (d) are shown in Figure 26. Weight percent is shown along the ordinate, and the depth from the sample surface is along the abscissa. The average  $H_2O$ ,  $O_2$ ,  $CO_2$ , and  $N_2$  concentrations are 0.5,



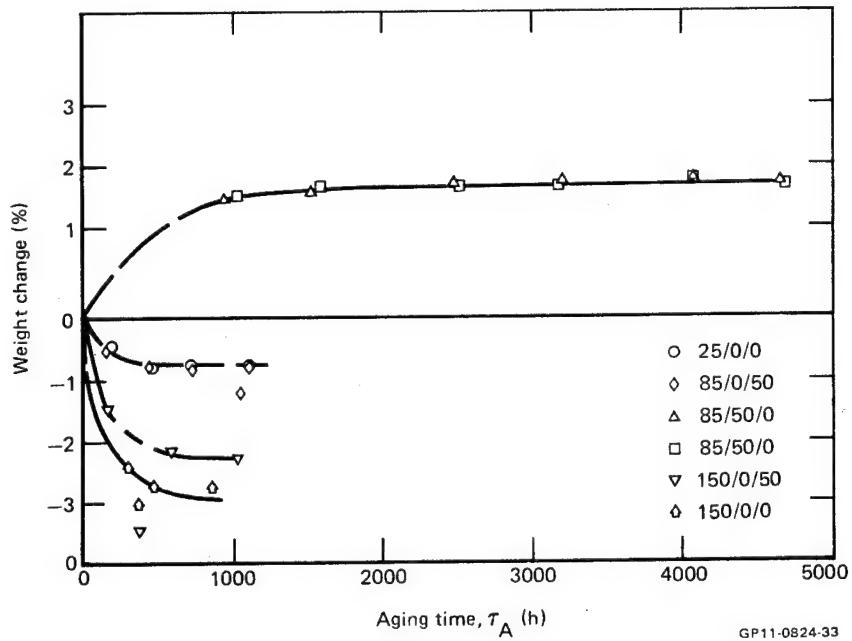
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Figure 26. Distribution of (a)  $H_2O$ , (b)  $O_2$ , (c)  $CO_2$ , and (d)  $N_2$  in unaged, cured MY720/Eporal resin as a function of distance from the top surface.

$< 1 \times 10^{-3}$ ,  $0.3 \times 10^{-3}$ , and  $4 \times 10^{-3}$  wt%, respectively. The amount of each of these compounds, especially  $H_2O$ , is relatively small. The water concentration is a function of both temperature and humidity and attains an equilibrium concentration of 2-3 wt% depending upon temperature, humidity, and stress (see Section 4.6).

#### 4.6 Gravimetric Analysis

The weights of the resin coupons prior to and after environmental aging were measured. The weight changes as a function of aging are summarized in Figure 27 where the weight gain or loss is given for coupons aged at  $85^{\circ}C$  in both humid (50% RH) and dry atmospheres in the presence and absence of external tensile stress (50% UTS). In addition, the weight loss for the samples aged in a dry atmosphere at  $150^{\circ}C$  in the presence and absence of external stress is shown in Figure 27. Samples exposed to a humid atmosphere readily sorb water; the equilibrium value at  $85^{\circ}C$  and 50% RH was approximately 1.8%. External mechanical stress had little effect on the equilibrium value, although other studies<sup>25</sup> indicate that the diffusion coefficient varies with applied stress. The samples aged in dry environments lost weight; the equilibrium weight loss for the samples aged at  $85^{\circ}C$  in a low humidity (~ 0% RH) atmosphere in the presence or absence of external stress was approximately 0.7%. The equilibrium weight loss for the samples aged at  $150^{\circ}C$  depends upon whether the applied stress and the losses were greater than can be accounted for by water alone. The equilibrium weight losses were approximately 2.3 and 3 wt% for the stressed (50% UTS) and unstressed samples, respectively. According to the PAMS measurements (see Section 4.5), the amount of  $H_2O$  in the initial samples was approximately 0.1%, but the resin readily sorbs water. The weight losses exhibited by the coupons in the low humidity environments must be due to the desorption of compound(s) other than water. The equilibrium weight gain for a coupon exposed to the ambient room conditions for 14 months was 0.5 wt% and reflects the fact that the average humidity in the laboratory varies from 10 to 40% during the year.



**Figure 27. Weight change of the resin exposed to different environmental conditions as a function of aging time. The symbols refer to aging temperature / % humidity / % UTS.**

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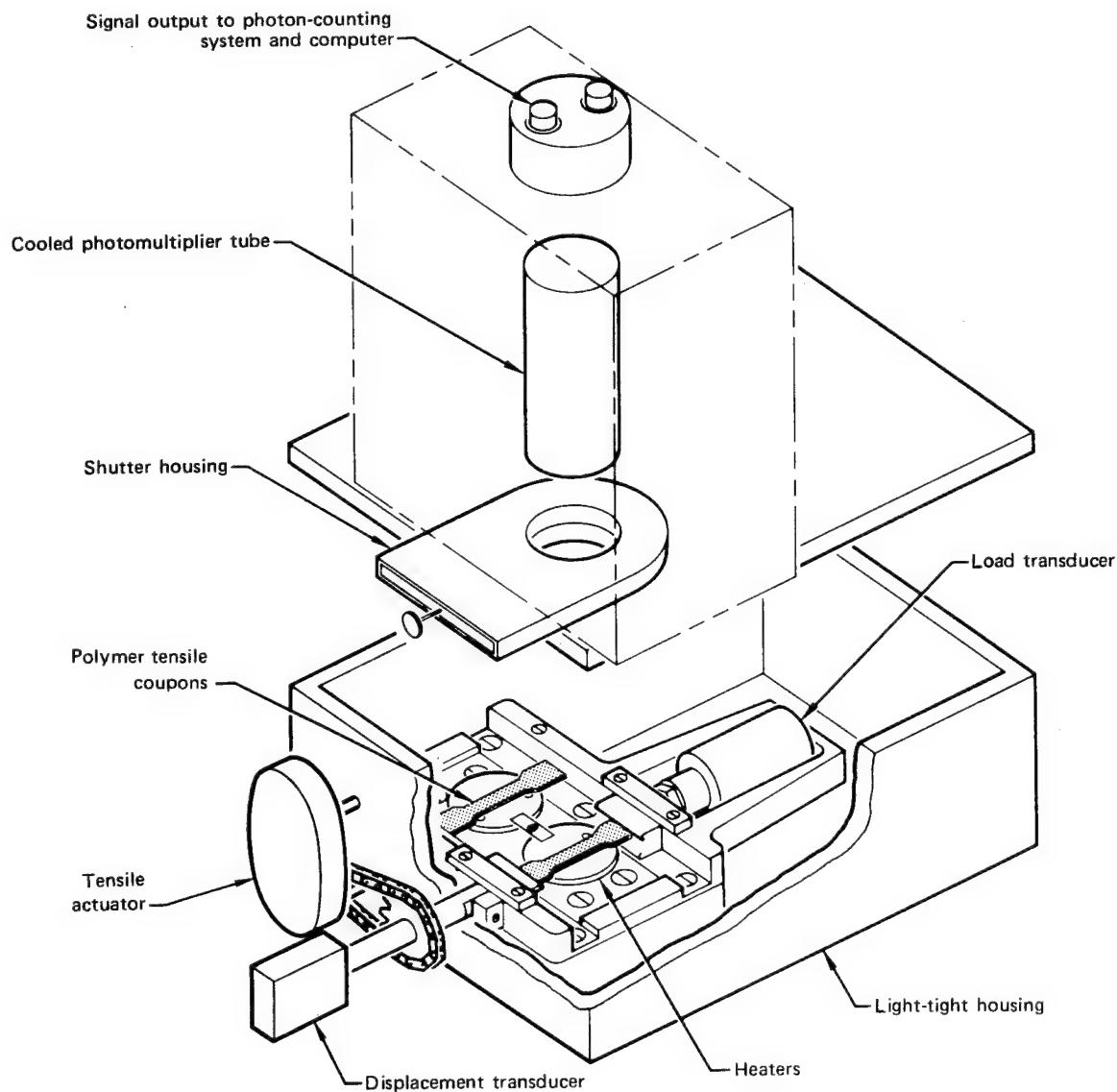
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## APPENDIX A: CHEMILUMINESCENCE SYSTEM

An exploded view of the chemiluminescence system designed and fabricated at MDRL is shown in Figure A1. Samples can be exposed to selected combinations of atmosphere, temperature, and tensile stress while measuring the luminescence resulting from exoergic reactions within the sample. Generally, air, oxygen, or nitrogen is used to purge the sample chamber; however, other gases can be used. The sample stage incorporates two matched heaters and



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Figure A1. Exploded view of the chemiluminescence system.

thermocouples to control temperatures up to 200°C. A gearmotor, belt, and worm-drive mechanism apply tensile stress to the sample through two grips attached to cylinders cast in the tensile coupons. Tensile loads up to 500 N can be applied to coupons, and loads are recorded by a transducer attached to the fixed grip. The photomultiplier tube (PMT) is coupled to the sample through a quartz dewar which thermally isolates the sample chamber from the cooled PMT. Electrical pulses from the PMT are processed by an amplifier/discriminator and counted for selected time periods by a photon counting system (E.G.&G., Princeton Applied Research models 1121 and 1112). Sample surface temperatures are measured directly by a thermocouple and digitized for data reduction and interpretation.

The system is controlled and the data are collected and analyzed by a microcomputer (Digital Equipment Co. MINC 23 with VT105 CRT terminal). The CL experiment variables, photon counts per second, sample temperature, stress, and strain, are monitored continuously by the computer (Figure A1) and recorded at selected intervals for closed-loop control of the CL experiment

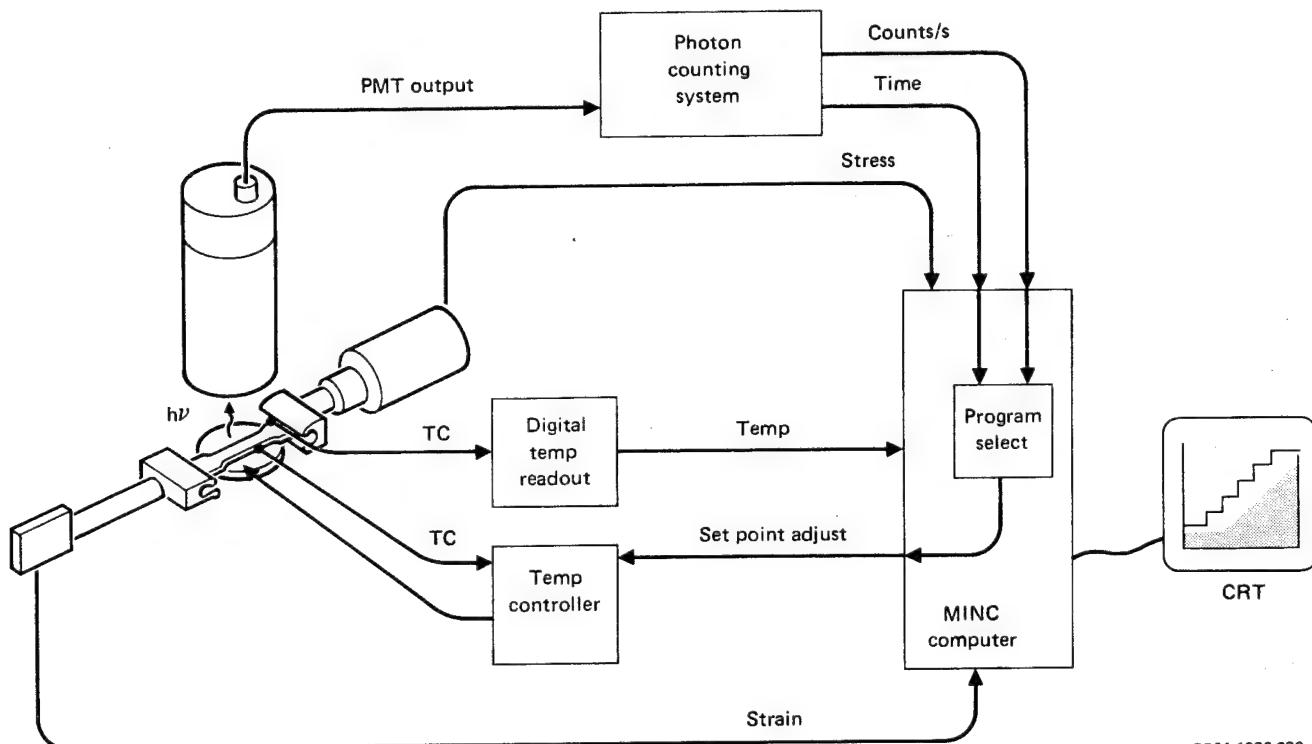


Figure A2. Block diagram of the CL system with microcomputer data handling and control system.

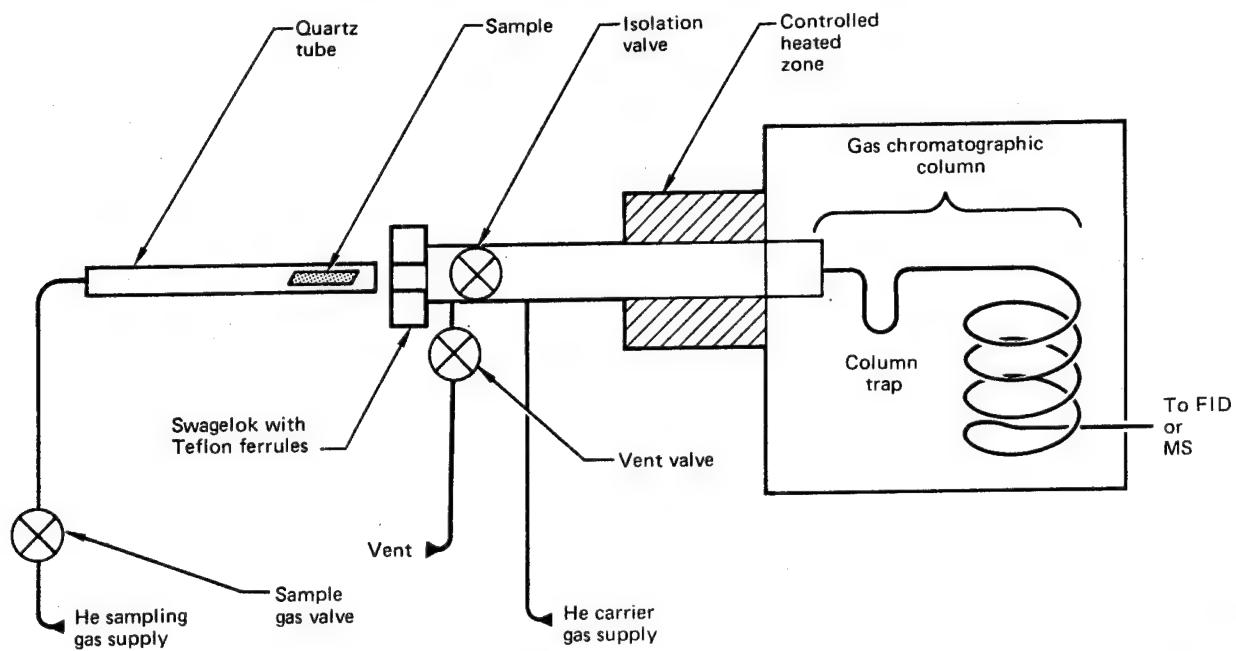
and subsequent off-line data storage on flexible disk. The computer is programmed to operate unattended; thus experiments can be performed overnight, greatly increasing the data output of the CL system. Sample temperatures are controlled by the computer based on either a given time interval or a plateau-detection algorithm.

## APPENDIX B: VAPORIZATION GAS CHROMATOGRAPHY/MASS SPECTROMETRY

The characterization of indigenous volatile compounds is performed with the gas chromatographic inlet shown schematically in Figure B1. The sample (typically 30-100 mg) is placed in a clean quartz tube (6 mm o.d. nominal), one end of which is attached to a source of helium (10 to 30 cm<sup>3</sup>/min). A quartz wool plug is used to prevent the sample from being blown out the end of the tube. The other end is connected to the isolation valve by a Swagelok connection using Teflon ferrules.

For 2 min after the quartz sample tube is connected, the sample is purged at room temperature by opening both the sample gas valve and the vent valve. During this time, the isolation valve is closed and the column trap U-tube is immersed in liquid nitrogen.

The indigenous volatile compounds in the sample vaporize when the quartz tube is inserted into the controlled heated zone; this procedure requires opening the isolation valve, closing the vent valve, loosening the Swagelok nut at the isolation valve, and pushing the sampling tube through the open isolation valve. The Swagelok nut at the isolation valve is tightened when the sampling tube is butted against the exit tube of the controlled-heat zone.



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Figure B1. Block diagram of vaporization GC sampling system.

Volatile compounds desorbed from the sample are then carried by the helium stream into the U-tube. The quartz sample tube is left in the hot zone for the desired length of time, typically 10 or 20 min. While the sample is heated, the carrier gas flows around the outside of the sampling tube and into the column trap. This precaution is necessary to ensure that desorbed volatile compounds are not back-flushed into the space between the outer wall of the quartz sampling tube and the inner wall of the hot zone.

After the sample has been heated for the desired time, the Swagelok nut at the isolation valve is loosened, and the sample tube is removed from the hot zone. The isolation valve is then shut, and the vent valve is opened. This status is maintained for a period of 2 min after heating to permit the flows in the system to equilibrate. The sampling gas supply is then shut off, and the vent is closed. Thus the quartz sample tube can be removed from the inlet, and a new sample can be loaded during the chromatographic analysis of the desorbed volatile compounds. If, on the other hand, it is desirable to heat the same sample again, the sampling tube is left in place while the sample remains under an atmosphere of helium.

During the entire desorption period, the U-trap is cooled to  $-196^{\circ}\text{C}$ . After the 2 min equilibrium following removal of the sample tube from the hot zone, the liquid nitrogen bath is removed from the trap and the temperature program of the chromatographic analysis is initiated. Typical operating conditions for the chromatographic analysis are shown in Table B1. A complete blank analysis with an empty sample tube is performed periodically to determine the background concentration of the compounds of interest.

TABLE B1. CONDITIONS USED IN VAPORIZATION GAS CHROMATOGRAPHIC ANALYSES.

● Hot zone temperature	● Variable within the range $125^{\circ}$ to $250^{\circ}\text{C}$
● Sampling period	● Variable in the range 1 to 60 min (usually 10 or 20 min)
● Sampling gas flow rate	● $15 \text{ cm}^3 \text{ atm/min}$
● Carrier gas supply (He)	● $3.3 \text{ cm}^3 \text{ atm/min}$
● Column Phase length diameter	● Carbowax 1540 15 m 0.5 mm
● Temperature program	● $4^{\circ}\text{C/min}$ to $135^{\circ}\text{C}$ , 20 min at $135^{\circ}\text{C}$

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## APPENDIX C: STRESS MASS SPECTROMETRY

Stress MS is a new, unique application of mass spectrometry to study the mechanical degradation of polymeric materials. The volatile compounds evolved during mechanical loading expand into the ion-source region of a mass spectrometer and are subsequently ionized and mass analyzed.

A time-of-flight mass spectrometer (TOFMS) is ideally suited for these experiments for several reasons: 1) the instrument has a large ion-source housing which readily accommodates the various devices for mechanically loading polymer samples, 2) the TOFMS has an open ion-source which permits easy entry of the evolved compounds into the ionizing region, and 3) the TOFMS produces mass spectra at the rate of 10 to 20 kHz, thereby permitting the analysis of a brief burst of compounds, as may occur when a material fails under load.

The standard TOFMS [Bendix (now CVC Products) model 12-101] was modified and upgraded for these experiments. Of particular interest are changes in the ion-source housing and operating electronics. The ion-source housing cross was designed and fabricated to locate the sample immediately behind a high-transmission grid which serves as the backing plate for the ion source to maximize ion efficiency. The entire electronic chassis of the TOFMS was upgraded with a Mark V solid-state chassis to increase the stability and reliability of the instrument.

A photograph of the new system, capable of stressing filaments, thin films, or dogbone coupons in a reproducibly controlled manner, is shown in Figure C1. A frame and lintel supports the upper sample clamp, and the lower sample clamp is attached to the shaft of a three-axis micropositioner. The Y-axis of the micropositioner is driven down, thereby loading the sample in tension. The velocity of the Y-axis motion can be selected from 3  $\mu\text{m/s}$  to 3000  $\mu\text{m/s}$  with loads up to 2000 N on the sample.

The evolution of compounds during loading and at the moment of failure is of particular interest in these experiments. Two different data acquisition techniques are used to acquire mass spectral data of the evolved compounds: 1) z-axis modulated mass spectra and 2) continuous ion monitoring.

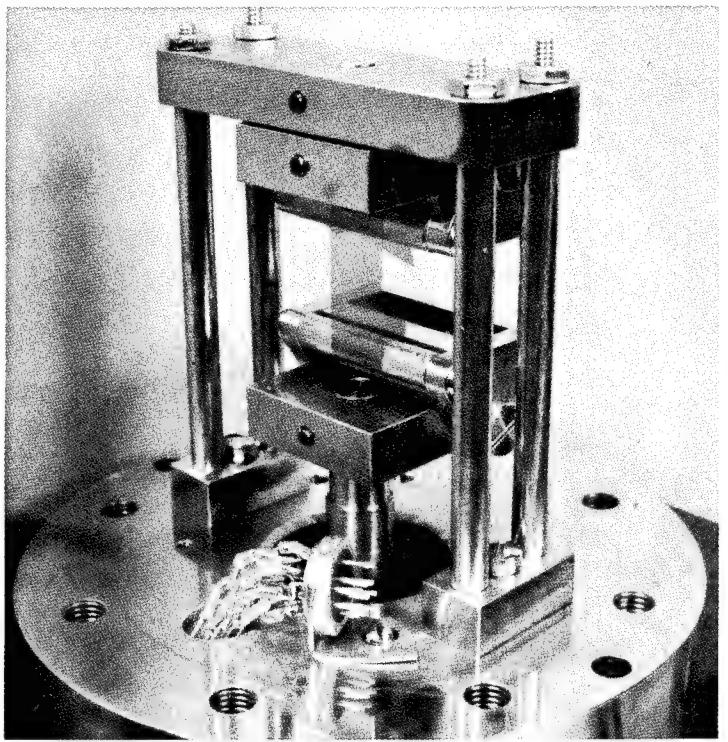


Figure C1. Precision tensile tester for SMS.

GP11-0824-47

z-Axis Modulated Mass Spectra: In this technique, oscilloscope photography is used to record a z-axis modulated display. The intensity of the mass spectral line controls the brightness of the line on the oscilloscope screen. The mass axis is displayed along the abscissa and the elapsed time along the ordinate. The separation between successive traces indicates the elapsed time from the beginning to the end of the trace. The number of traces displayed can range from 2 to 16, and the duration of each trace can range from 1.6 ms to 6.6 s. This technique is particularly useful for acquiring data from the brief burst of volatile compounds evolved upon failure of a sample loaded in tension. This data acquisition technique is strictly qualitative.

Continuous Ion Monitoring: If, from previous experiments, the identity of evolved compounds is known, then one or more ions characteristic of these compounds can be monitored continuously with a four-channel monitor (CVC MA006). There are two such monitors in this system, thus permitting the continuous recording of eight separate ions during the course of an experiment. This data acquisition technique is useful to monitor the evolution of a compound as the polymeric material is mechanically loaded.

#### APPENDIX D: PRECISION ABRASION MASS SPECTROMETRY

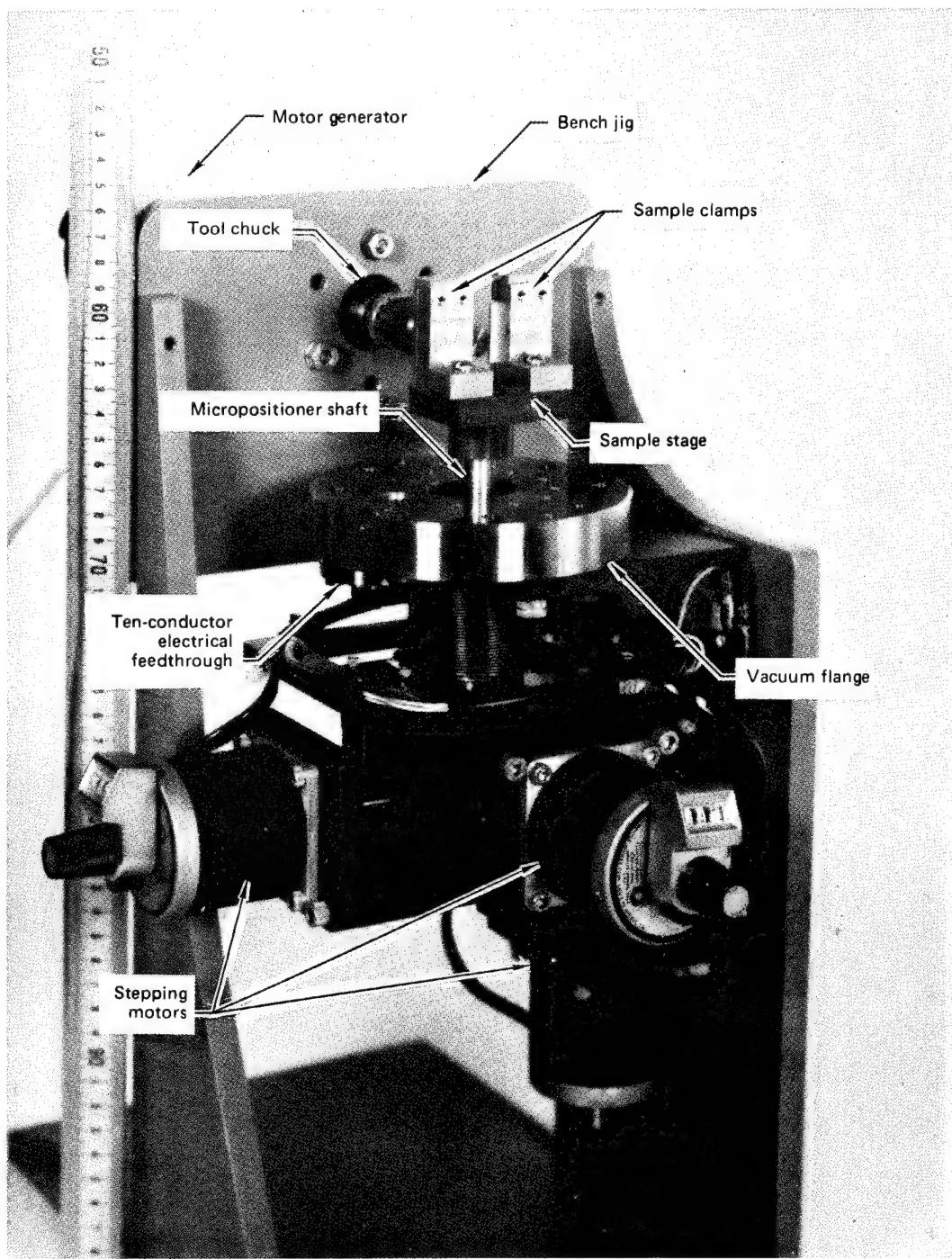
During PAMS analyses a composite or polymeric material is abraded inside the ion-source housing of a time-of-flight mass spectrometer (upgraded Bendix model 12). A photograph of the PAMS inlet system is shown in Figure D1. The sample is mounted to the stage at the end of the three-axis micropositioner shaft. Each of the mutually perpendicular axes is driven by a stepping-motor lead-screw system which permits accurate positioning of the sample stage with respect to the tool tip to within  $3 \mu\text{m}$  ( $1.25 \times 10^{-4}$  in.). The stepping motors can drive the stage at velocities ranging from 0 to 3 mm/s. Control of these motors is accomplished by time-sharing a stepping-motor controller and an indexing motor driver.

The tool drive system is mounted along one of the three principal axes of the micropositioner. Rotary power to the precision tool chuck (Albrecht) is provided by a motor generator which maintains the selecting cutting speed for torque loads to the tool up to  $0.5 \text{ N} \cdot \text{m}$ . Tool speed can be varied continuously from 3 to 3000 revolutions/min.

Abrasion of the sample is performed by driving the sample into the tool using the micropositioner. A selection of tungsten-carbide and diamond-grit tools is available for abrading the resin. Both the micropositioner and the tool drive system include mechanical vacuum feedthroughs which were chosen expressly for their low outgassing characteristics.

A modular instrumentation microcomputer (Digital Equipment Corporation MINC) is used to acquire and process mass spectral data from the PAMS experiments. The hardware used in this facility is shown in Figure D2.

The multiplexer permits the use of one analog-to-digital card to convert all of the analog information from the mass spectrometer to digital form. In this system, all voltage signals from the analog scanner, total ion integrator, and the four-channel monitors are input through the multiplexer. In addition, 10 signals which monitor the electronic condition of the chassis of the TOFMS are available for recording through the multiplexer analog-to-digital converter combination. Another 10 channels are available to accommodate future data acquisition needs.



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Figure D1. Precision abrasion inlet system mounted in bench jig.

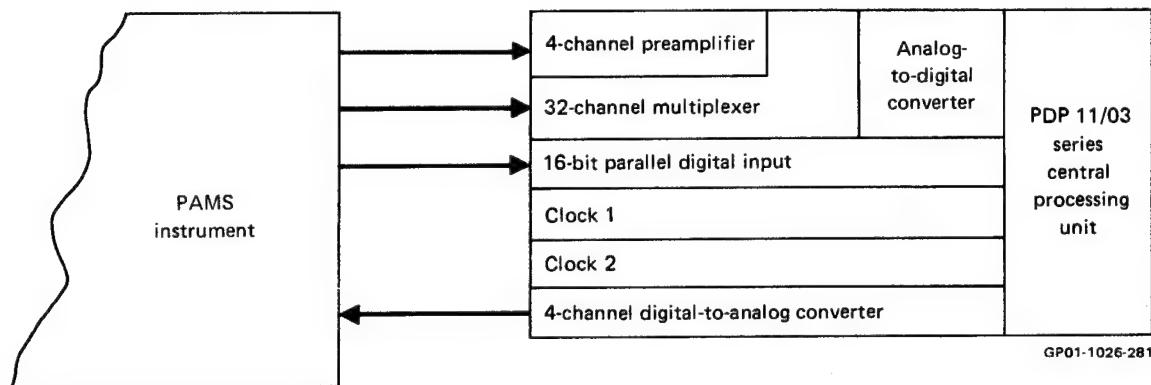


Figure D2. MINC interface modules for the PAMS system.

The digital input card is used to record the digital output of an ionization gauge controller (Veeco) which monitors the vacuum in the mass spectrometer. The controller uses only half of the capacity of the digital-input card.

The clock modules are used to control the rate at which data are acquired and to provide a digital signal to drive the stepping motor of the PAMS device. The digital-to-analog converter is used to condition the signal sent to the stepping-motor drive unit.

This hardware configuration permits acquisition of all pertinent data from a PAMS experiment and control of the sample-stage movement by the central processing unit (PDP 11/03). This arrangement increases the precision with which the abrasion process is controlled and represents an improvement in the accuracy of averaging the results from several holes into one concentration profile.

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